5 Cyclopentadienyl Amido Zirconium Chloride and Carbyl Complexes; Synthesis and Reactivity of $[C_5H_4(CH_2)_nNR]ZrX_2$.*

5.1 Introduction.

Zirconocene complexes are increasingly important in catalysis, especially in catalytic polymerization of α-olefins[1] and show in general higher activities than the analogous titanocene or hafnocene compounds.[1b] Some years ago, the development of new catalysts based on linked cyclopentadienyl amido group 4 metal complexes $[C_5R_4\text{-}Y\text{-}NR']MCl_2$ (R= H, Me; Y = $SiMe_2$, $(SiMe_2)_2$, $(CH_2)_2$; R' = *t*-Bu, aryl; M = Ti, Zr) by Dow Chemical and Exxon Chemical[2] gave a strong stimulus for further development of this area. This however, by the time we started this project, has been mainly focused to titanium complexes bearing a relatively narrow class of silyl bridged Cp-amido ligands. For zirconium and hafnium, only a limited number of $SiMe_2$ or otherwise bridged Cp-amido complexes have been described so far and little is known about the more general chemistry of these complexes.[3]

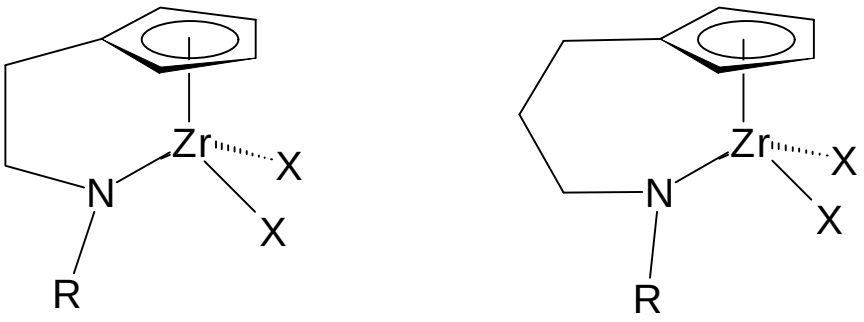


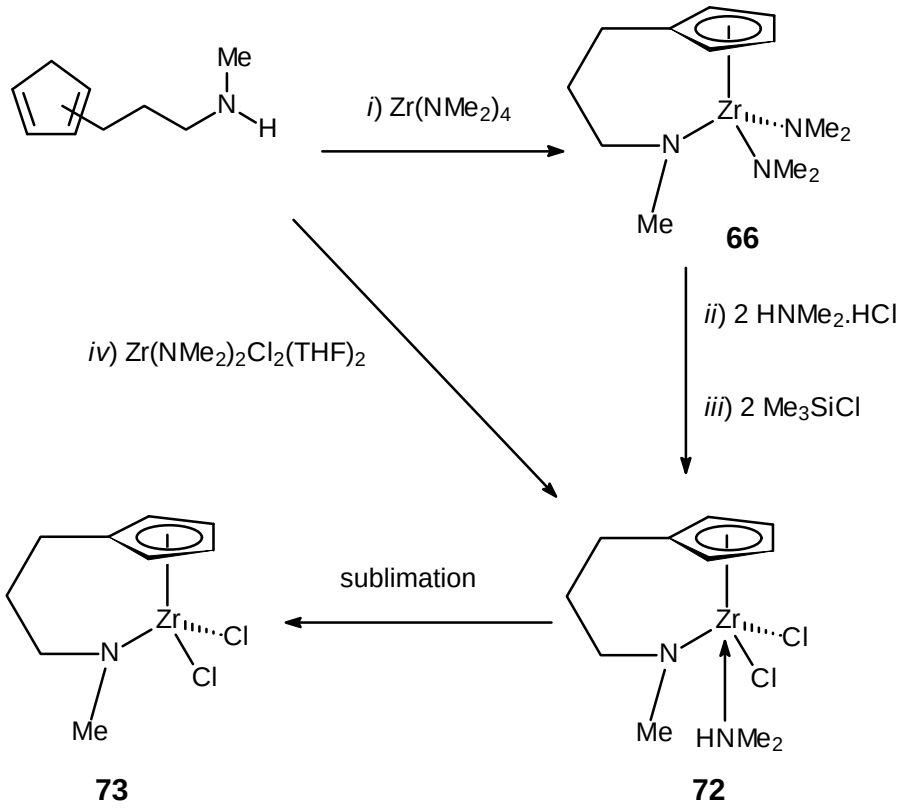
Figure 1.

* *Parts of this work have been performed in collaboration with K. Liekelema, A. Arnold and M. Bouwkamp.*

In order to extend the Cp-amido titanium chemistry described in the previous chapters, we felt it would be worth to explore the analogous zirconium complexes (Figure 1).

5.2 Synthesis and Characterization of Cyclopentadienyl Amido Zirconium Dichlorides $[C_5H_4(CH_2)_nNR]ZrCl_2$.

Attempts to synthesize $[C_5H_4(CH_2)_nNR]ZrCl_2$ complexes using the same route as described for the $[C_5H_4(CH_2)_nNR]TiCl_2$ compounds (Chapter 2) were not successful as unidentifiable oily products were obtained.[4] Aminolysis of homoleptic metal amides, first described by Lappert,[5] appeared to be a better route to introduce Cp-amido ligands to zirconium.[3a,6] For example $[C_5H_4(CH_2)_3NMe]Zr(NMe_2)_2$ was prepared by reacting $Zr(NMe_2)_4$ with the amino-cyclopentadiene, $C_5H_5(CH_2)_3N(H)Me$ (Scheme 1, *i*).[3a] Conversion of such Cp-amido zirconium bis(dimethylamido) complexes to the corresponding dichloro complexes was carried out by reacting the metal amides with $HNMe_2$.HCl (Scheme 1, *ii*). In our experiments, this method gave irreproducible results and often mixtures of products were obtained. Recently Petersen *et al.* developed an elegant route to convert bis-amido complexes to dichlorides using Me_3SiCl.[6] This appeared to be very useful for our systems as well (Scheme 1, *iii*). Independently, we developed an alternative amine-elimination route starting from the mixed bis-amido zirconium dichloride $Zr(NMe_2)_2Cl_2(THF)_2$ (**59**) directly yielding the dichloro complex in a one step synthesis (Scheme 1, *iv*).


Me
N
H
i) $Zr(NMe_2)_4$
Zr
NMe_2
N
NMe_2
Me
66
ii) 2 $HNMe_2$.HCl
iii) 2 Me_3SiCl
iv) $Zr(NMe_2)_2Cl_2(THF)_2$
sublimation
Zr
Cl
N
Cl
Me
73
Zr
Cl
N
Cl
Me
$HNMe_2$
72

Scheme 1.

The introduction of cyclopentadienyl and amido moieties proceeds at different rates. The cyclopentadiene function reacts faster than the amino function with metal amides (^{1}H-NMR). The reactivity of the ligands towards a metal amide depends strongly on the zirconium precursor. For $Zr(NMe_2)_4$ and $C_5H_5(CH_2)_2N(H)$-t-Bu the reaction was complete within 1 h at 50 ^oC (NMR). $Zr(NMe_2)_2Cl_2(THF)_2$ needed more drastic conditions (75 ^oC, 16 h). The $[C_5H_4(CH_2)_nNR]Zr(NMe_2)_2$ complexes (n = 2, R = Me, *t*-Bu; **64**, **65**; n = 3, R = Me, Ad; **66**, **69**) were purified by vacuum distillation and isolated as light green oils in 72-90% yield. With Me_3SiCl (2 eq.) these bis(amido) complexes were cleanly converted into the corresponding dichlorides (**70**-**77**) (Scheme 1, *iii*). The dichlorides could also be prepared in a one pot synthesis by subsequent addition of Me_3SiCl without isolation of the bis(dimethylamido) complexes. The yields thus obtained are comparable to those of the one step synthesis using $Zr(NMe_2)_2Cl_2$.2THF (**63**) (Scheme 1, *iv*, 60-80%). Both routes resulted in formation of the dimethylamine adduct $[C_5H_4(CH_2)_nNR]ZrCl_2(Me_2NH)$, but the Lewis-base free products (**70**-**77**) were obtained by vacuum sublimation.

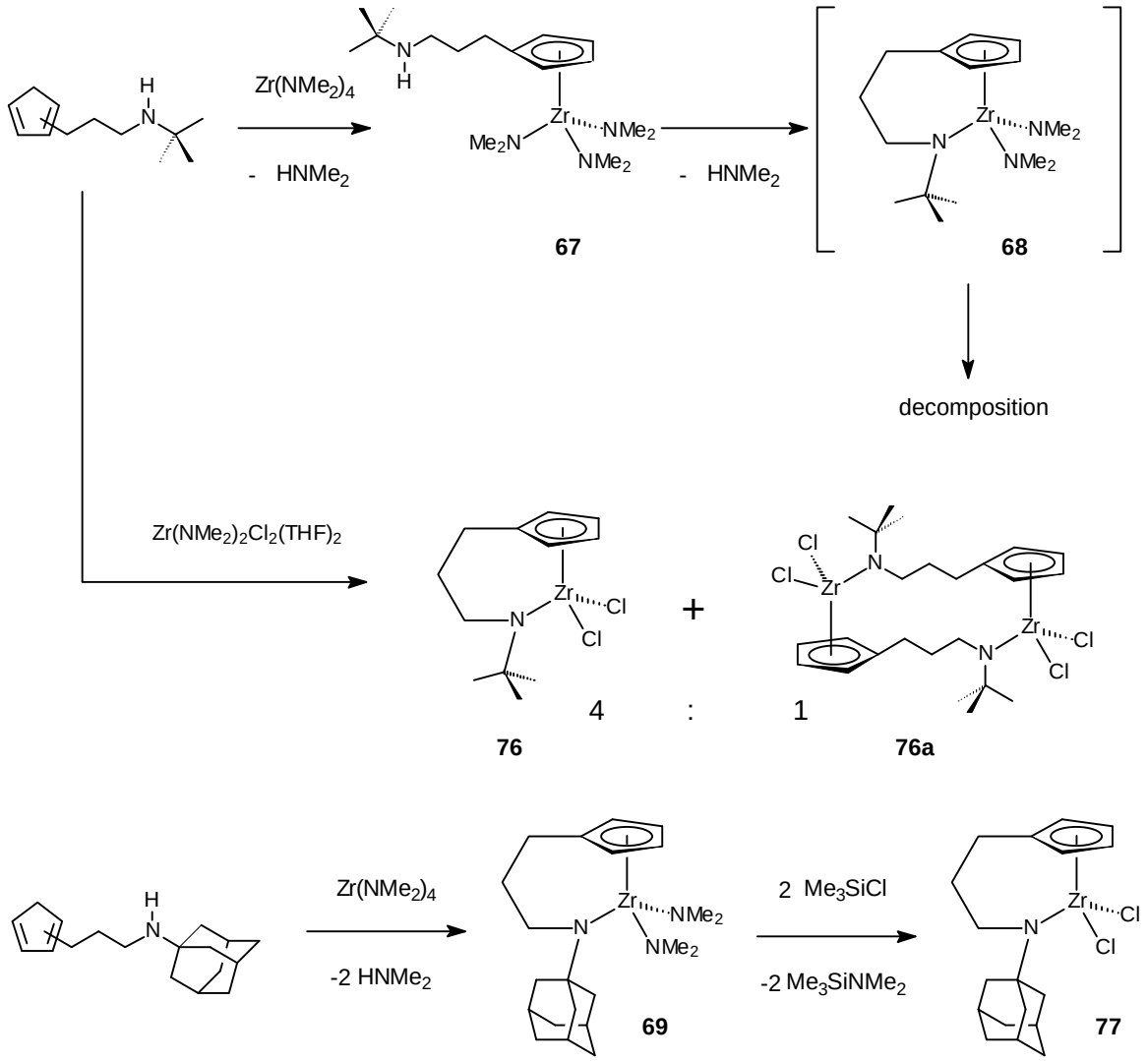
Table 1. Cp-amido Zirconium complexes

Compound	method	yield (%)
$[C_5H_4(CH_2)_2NMe]Zr(NMe_2)_2$ (**64**)	*i*	72
$[C_5H_4(CH_2)_2N$-*t*-Bu$]Zr(NMe_2)_2$ (**65**)	*i*	80
$[C_5H_4(CH_2)_3NMe]Zr(NMe_2)_2$ (**66**)	*i*	90[a]
$[C_5H_4(CH_2)_3N(H)$-*t*-Bu$]Zr(NMe_2)_3$ (**67**)	*i*	90
$[C_5H_4(CH_2)_3N$-*t*-Bu$]Zr(NMe_2)_2$ (**68**)	*i*	[b]
$[C_5H_4(CH_2)_3NAd]Zr(NMe_2)_2$ (**69**)	*i*	46
$[C_5H_4(CH_2)_2N$-*i*-Pr$]ZrCl_2$ (**70**)	*i+iii/iv*	74
$[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrCl_2$ (**71**)	*i+iii/iv*	69
$[C_5H_4(CH_2)_3NMe]ZrCl_2$ (**73**)	*i+iii*	68
$[C_5H_4(CH_2)_3NEt]ZrCl_2$ (**74**)	*i+iii*	66
$[C_5H_4(CH_2)_3N$-*i*-Pr$]ZrCl_2$ (**75**)	*i+iii/iv*	65/71
$[C_5H_4(CH_2)_3N$-*t*-Bu$]ZrCl_2$ (**76**)	*iv*	59
$[C_5H_4(CH_2)_3NAd]ZrCl_2$ (**77**)	*i+iii*	46

[a]) ref 7; [b]) could not be isolated.

A wide range of Cp-amido ligands can be introduced on zirconium using these methods (Table 1).[6,8] Only for the sterically least hindered aminocyclopentadiene, $C_5H_5(CH_2)_2N(H)Me$, the desired dichloride could not be obtained. Although aminolysis of $Zr(NMe_2)_4$ did result in $[C_5H_4(CH_2)_2NMe]Zr(NMe_2)_2$ (**64**), subsequent reaction with Me_3SiCl gave ill defined products. With $Zr(NMe_2)_2Cl_2(THF)_2$ similar results were obtained. The products are poorly soluble even in coordinating solvents such as THF. This suggests that higher aggregates of $[C_5H_4(CH_2)_2NMe]ZrCl_2$ have been formed. Sterically more demanding Cp-amido ligands, e.g. those containing long backbones in combination with bulky nitrogen substituents, give unexpected reactions as well. The reaction of $C_5H_5(CH_2)_3N(H)$-*t*-Bu with $Zr(NMe_2)_4$ at room temperature ceased with the formation of $[C_5H_4(CH_2)_3N(H)$-*t*-Bu$]Zr(NMe_2)_3$ (**67**). Under more forcing conditions (120 ^oC, 80 h) bonding of the amine function was observed yielding $[C_5H_4(CH_2)_3N$-*t*-Bu$]Zr(NMe_2)_2$ (**68**) (NMR), but competitive decomposition (evolution of *iso*-butene) prevented isolation of the complex. A key-feature of the thermolysis of Cp-amido group 4 metal complexes containing a *t*-butyl amido substituent appears to be activation of the *t*-butyl group resulting in evolution of *iso*-butene (Chapter 3). A more detailed thermolysis study is presented elsewhere in this chapter. To circumvent amido activation is using substituents in which activation is inhibited. The, with respect to $[C_5H_4(CH_2)_3N$-*t*Bu], sterically/electronically comparable adamantyl substituted ligand $[C_5H_4(CH_2)_3NAd]$ is a good alternative, since formation of a C=C double bond is highly disfavored in the adamantyl cage. The reaction of $Zr(NMe_2)_4$ with $C_5H_5(CH_2)_3N(H)Ad$ does indeed give the desired complex $[C_5H_4(CH_2)_3NAd]Zr(NMe_2)_2$ (**69**) in fair yield (Scheme 2). Subsequent reaction with 2 eq. of Me_3SiCl also affords the dichloro complex $[C_5H_4(CH_2)_3NAd]ZrCl_2$ (**77**).

With $Zr(NMe_2)_2Cl_2(THF)_2$ as precursor $C_5H_5(CH_2)_3N(H)$-*t*-Bu yielded a mixture of two products in a ratio of 4 : 1. The major product was identified as $[C_5H_4(CH_2)_3N$-*t*-Bu$]ZrCl_2$ (**76**) on the basis of the close similarity of the ^1H- and ^{13}C NMR spectra with those of other propylene bridged complexes (Table 2). The ^1H NMR resonances of the minor product are shifted up-field compared to the major product and the features of the resonances of the backbone differ clearly from those observed for the major product. The internal methylene group of the backbone appears as regular quintet whereas a complex multiplet is observed for all other C_3 bridged complexes. This indicates that the backbone is more flexible and allows the internal methylenes to rotate freely. On the basis of these spectral data a dimeric species $\{[C_5H_4(CH_2)_3N$-*t*-Bu$]ZrCl_2\}_2$ (**76a**) is postulated with the amido function bonded to the other metal center (Scheme 2).



Scheme 2.

The dichlorides (Table 1) are fairly well soluble in THF, $CHCl_3$ and aromatic solvents. The compounds with small nitrogen substituents (Me, Et) are sparingly soluble in aromatic solvents (benzene, toluene). In contrast to $\{[C_5H_4SiMe_2N\text{-}t\text{-}Bu]ZrCl(\mu\text{-}Cl)\}_2$, which was found to be dimeric in both the solid state and in solution (NMR),[8,9] the ethylene bridged complex $[C_5H_4(CH_2)_2N\text{-}t\text{-}Bu]ZrCl_2$ is a monomer. Also the N-*i*-Pr compound $[C_5H_4(CH_2)_2N\text{-}i\text{-}Pr]ZrCl_2$ is monomeric in solution. The C_3-bridged complexes $[C_5H_4(CH_2)_3NMe]ZrCl_2$ (**73**) and $[C_5H_4(CH_2)_3NEt]ZrCl_2$ (**74**), are poorly soluble in benzene and probably are dimers. The X-ray structure of $\{[C_5H_4(CH_2)_3NMe]ZrCH_2Ph(\mu\text{-}Cl)\}_2$[3a] confirms this, although NMR spectra ($CDCl_3$) of the dichlorides **73** and **74** suggest C_s symmetry.

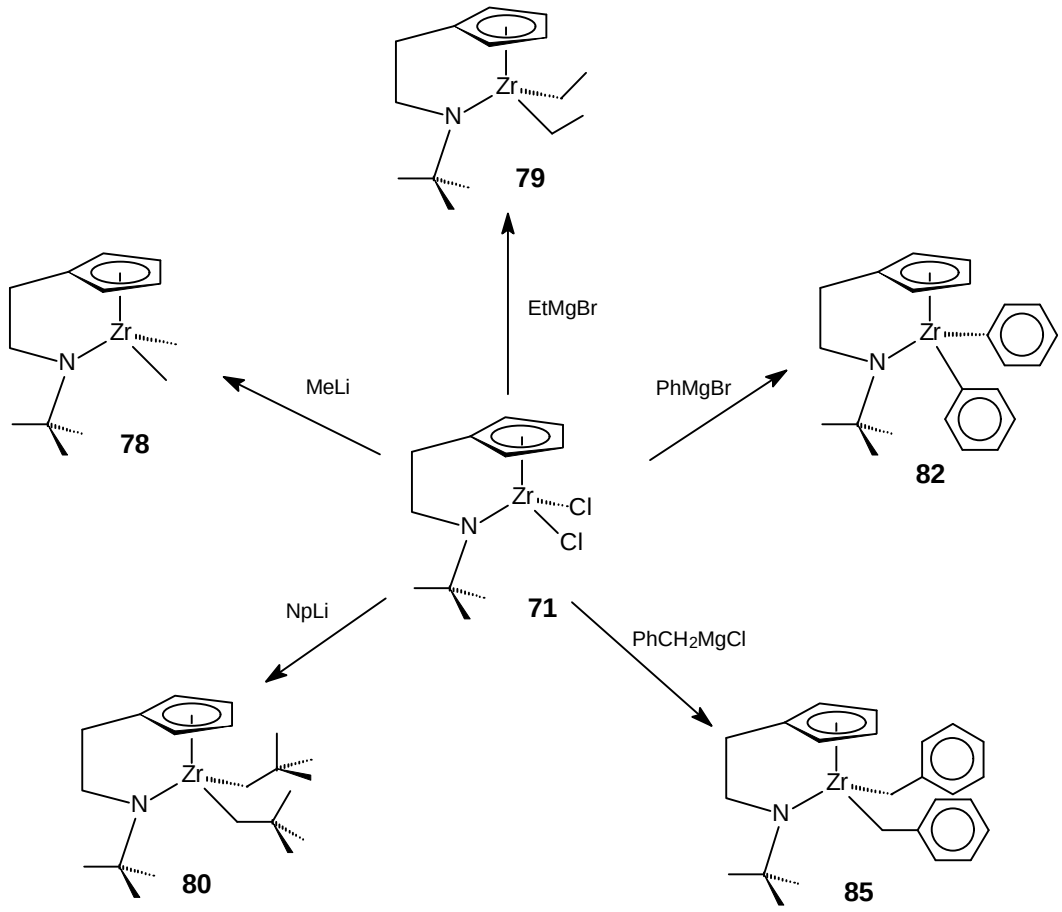
5.3 Synthesis and Characterization of Cp-amido Zirconium Bis(carbyl) Complexes $[C_5H_4(CH_2)_nNR]ZrR'_2$.

The Cp-amido zirconium dichlorides are excellent precursors for bis(alkyl) and bis(aryl) complexes of which a range has been synthesized (Table 2). Attention has been focused on $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrR_2$ (R = Me, Et, CH_2CMe_3, Ph, CH_2Ph) and $[C_5H_4(CH_2)_nNR]Zr(CH_2Ph)_2$ (n = 2, 3; R = Me, Et, *i*-Pr, *t*-Bu) complexes for comparison with the titanium analogues. The complexes were prepared by treatment of ether suspensions of the dichlorides with appropriate organo lithium or Grignard reagents (Scheme 3). The carbyl complexes are crystalline compounds (70-85% yield), except $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrMe_2$ (**78**), $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrEt_2$ (**79**) and $[C_5H_4(CH_2)_3N$-*t*-Bu$]Zr(CH_2Ph)_2$ (**89**) which were isolated as oils.

Table 2. Cp-amido zirconium carbyl complexes $[C_5H_4(CH_2)_nNR]ZrR'_2$.

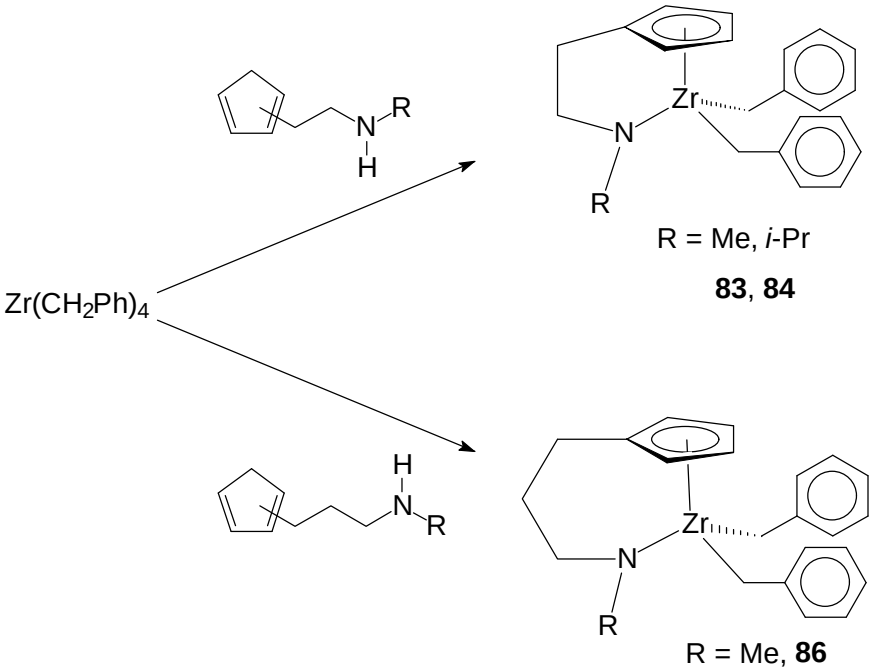
compound	yield (%)	color	cryst./oil
$[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrMe_2$ (**78**)	87	white	oil
$[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrEt_2$ (**79**)	86	white	oil
$[C_5H_4(CH_2)_2N$-*t*-Bu$]Zr(CH_2CMe_3)_2$ (**80**)	68	white	cryst.
$[C_5H_4(CH_2)_2N$-*i*-Pr$]ZrPh_2$ (**81**)	45	light brown	cryst.
$[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrPh_2$ (**82**)	55	light brown	cryst.
$[C_5H_4(CH_2)_2NMe]Zr(CH_2Ph)_2$ (**83**)	22	brown yellow	cryst.
$[C_5H_4(CH_2)_2N$-*i*-Pr$]Zr(CH_2Ph)_2$ (**84**)	65	brown yellow	cryst.
$[C_5H_4(CH_2)_2N$-*t*-Bu$]Zr(CH_2Ph)_2$ (**85**)	65	yellow	cryst.
$[C_5H_4(CH_2)_3NMe]Zr(CH_2Ph)_2$ (**86**)	90[a]	yellow	cryst.
$[C_5H_4(CH_2)_3NEt]Zr(CH_2Ph)_2$ (**87**)	65	yellow	cryst.
$[C_5H_4(CH_2)_3N$-*i*-Pr$]Zr(CH_2Ph)_2$ (**88**)	85	yellow	cryst.
$[C_5H_4(CH_2)_3N$-*t*-Bu$]Zr(CH_2Ph)_2$ (**89**)	77	orange	oil

[a]) NMR tube experiment.



Scheme 3.

Introduction of ligands by proteolysis of homoleptic metal alkyls[10] is an interesting alternative for the synthesis of linked Cp-amido metal carbyl complexes. For group 4 metals several homoleptic metal alkyls, MR_4 (M = Ti, Zr, Hf; R = CH_2CMe_3,[11] CH_2SiMe_3,[12] CH_2Ph,[13] norbornyl[14]) and mixed metal alkyl chlorides, $M(R)_xCl_{3-x}$ are known.[15] When $Zr(CH_2Ph)_4$ was reacted with $C_5H_5(CH_2)_2N(H)Me$ at room temperature (16 h), formation of the bis-benzyl complex $[C_5H_4(CH_2)_2NMe]Zr(CH_2Ph)_2$ (**83**) and 2 eq. of toluene (NMR) was observed (Scheme 4). The sterically more demanding neutral ligands like $C_5H_5(CH_2)_3N(H)Me$ and $C_5H_5(CH_2)_2N(H)$-*i*-Pr required somewhat more drastic conditions (resp. 5 and 16 h at 50 ^oC). However, this route appeared less satisfactorily for $C_5H_5(CH_2)_3N(H)$-*i*-Pr and $C_5H_5(CH_2)_2N(H)$-*t*-Bu. Besides liberation of toluene, complex product mixtures were obtained (NMR). Apparently, the introduction of these ligands require such harsh conditions (> 80 ^oC, 24 h), that thermal decomposition of $Zr(CH_2Ph)_4$ interferes. Nevertheless, this method is a suitable entry for the chemistry of $[C_5H_4(CH_2)_2NMe]ZrR_2$ compounds since the corresponding dichloro precursor, $[C_5H_4(CH_2)_2NMe]ZrCl_2$, is not available (*vide supra*).



Scheme 4.

5.4 Stability of Cp-Amido Zirconium bis(Carbyl) Compounds $[C_5H_4(CH_2)_nNR]ZrR'_2$.

With exception of $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrEt_2$ (**79**), the bis(carbyl) complexes are fairly stable. They can be stored at room temperature although the bis(methyl) **78** is light sensitive and has to be stored in the dark. Noteworthy is the surprising stability of $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrEt_2$ (**79**) which can be isolated as a colorless oil but decomposes at ambient temperature ($t_{1/2}$ = 75 min at T = 25 ^oC). Complex **79** is clearly much more stable than $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiEt_2$ which decomposes already at -40 ^oC and Cp_2ZrEt_2 which has to be stored at -80 ^oC.[16]

5.5 Spectroscopic Characterization.

The ^1H and ^{13}C NMR spectra of the dichlorides $[C_5H_4(CH_2)_nNR]ZrCl_2$ **70**-**77** showed the same general features as those of the titanium complexes. The same trends were observed on elongation of the backbone and variation of the nitrogen substituent (Table 3). In the case of $[C_5H_4(CH_2)_2N$-*i*-Pr$]ZrCl_2$ (**70**) and $[C_5H_4(CH_2)_3N$-*i*-Pr$]ZrCl_2$ (**75**), substantial down-field shifts of the methine protons were observed (resp. 4.43 and 4.86 ppm) although the shifts are considerable smaller than those of the titanium analogues $[C_5H_4(CH_2)_2N$-*i*-Pr$]TiCl_2$ (**3**) and $[C_5H_4(CH_2)_3N$-*i*-Pr$]TiCl_2$ (**9**) (resp. 5.92 and 6.57 ppm, Chapter 2).

The larger atomic radius of zirconium readily explains the smaller down-field shifts observed for the methine protons in **70** and **75**. The smaller Cp-Zr-N bite-angle (107.6°) in {[$C_5H_4(CH_2)_3$NMe]ZrCH_2Ph(μ-Cl)}$_2$ compared to [$C_5H_4(CH_2)_3$N-*i*-Pr]TiCl_2) (112.6°) pulls the nitrogen substituent further away from the metal center. However, the rather small $^1J_{CH}$ coupling constant (117.2 Hz *vs* 128.9 Hz for the titanium analogue) observed for the methine carbon in [$C_5H_4(CH_2)_3$N-*i*-Pr]ZrCl_2 (**75**) could indicate a β-agostic interaction. For the C_2 bridged complex [$C_5H_4(CH_2)_2$N-*i*-Pr]ZrCl_2 (**70**) a higher $^1J_{CH}$ value is observed (129.4 Hz). The chemical shifts of the Cp-CH_2 protons of [$C_5H_4(CH_2)_3$N-*t*-Bu]ZrCl_2 (**76**) and [$C_5H_4(CH_2)_3$NAd]ZrCl_2 (**77**) are shifted down-field with respect to the NCH_2 protons. This is probably related to the steric bulk of the *t*-butyl and adamantyl groups, since this order is reversed in all other dichloro complexes.

Table 3. ^{1}H NMR data of [$C_5H_4(CH_2)_n$NR]ZrCl_2 complexes.[a]

Compound	C_5H_4	NCH_2	$-CH_2-$	Cp-CH_2	R, α	R, β
[$C_5H_4(CH_2)_2$N-i-Pr]ZrCl_2 (**70)**	6.3, 6.3	4.12		3.02	4.43	1.13
[$C_5H_4(CH_2)_2$N-t-Bu]ZrCl_2 (**71**)	6.38, 6.32	4.09		2.92		1.25
[$C_5H_4(CH_2)_3$NMe]ZrCl_2 (**73**	6.46, 6.05	2.95	2.17	2.80	3.27	
[$C_5H_4(CH_2)_3$NEt]ZrCl_2 (**74**)	6.52, 6.02	2.92	2.15	2.81	3.81	1.21
[$C_5H_4(CH_2)_3$N-i-Pr]ZrCl_2 (**75**)	6.52, 5.98	2.85	2.09	2.79	4.86	1.23
[$C_5H_4(CH_2)_3$N-t-Bu]ZrCl_2 (**76a**)[b]	6.51, 6.12	2.73	1.90	3.15		1.55
[$C_5H_4(CH_2)_3$N-t-Bu]ZrCl_2 (**76b**)[b]	6.27, 6.19	2.67	1.69	2.55		1.06
[$C_5H_4(CH_2)_3$NAd]ZrCl_2 (**77**)	6.47, 6.12	2.70	1.85	3.15		

[a]) 300 MHz, $CDCl_3$, 25 °C. [b]) **76a** major compound, **76b** minor compound.

The ^{1}H and ^{13}C NMR spectra (Table 4 and 5) of the carbyl complexes show the same general features as their titanium analogues. The α-protons of the diethyl, bis(benzyl) and bis(neopentyl) are diastereotopic and appear as well separated double doublets.

Organometallic benzyl complexes can release electronic unsaturation of the metal through η^2- or η^3-coordination of the benzyl ligand.[17] This type of coordination shows characteristic high-field shifts of the *ortho* protons and the benzylic carbon and large $^1J_{CH}$ values (Chapter 3).[18] The ^{1}H and ^{13}C NMR spectra of the bis-benzyl complexes (Table 4, 5), exhibit some interesting trends. Complexes with sterically more demanding Cp-amido ligands show smaller upfield shifts of the *o*-Ph protons. The ^{13}C NMR spectra show little variation of the

chemical shifts of the benzylic carbons (around 50 ppm), except for $[C_5H_4(CH_2)_3N$-*t*-Bu]$Zr(CH_2Ph)_2$ (**89**) with a Zr-CH_2 resonance at 63.53 ppm.

Table 4. ^{1}H-NMR data for $[C_5H_4(CH_2)_nNR]Zr(CH_2Ph)_2$.[a]

comp	Cp	NCH_2	CH_2-	Cp-CH_2	R, α	R, β	$ZrCH_2$	Ph o-H	Ph m-H	Ph p-H
79	5.72 5.28	3.43		2.43	2.49		1.44, 1.36	6.47	7.11	6.92
80	5.72 5.27	3.48		2.44	3.57	0.94	1.67, 1.05	6.58	7.12	6.94
81	5.57 5.47	3.35		2.24		1.13	1.94, 1.43	6.70	7.11	6.93
82	5.58 5.39	2.48	1.54	2.19	2.66		1.62, 1.26	6.58	7.11	6.93
83	5.60 5.39	2.45	1.53	2.21	3.05	1.00	1.62, 1.22	6.61	7.11	6.94
84	5.59 5.30	2.50	1.58	2.23	4.00	1.12	1.86, 1.01	6.70	7.14	6.95
85	5.79 5.52	2.10	1.31	2.58		1.20	2.15, 1.96	6.92	7.21	6.92

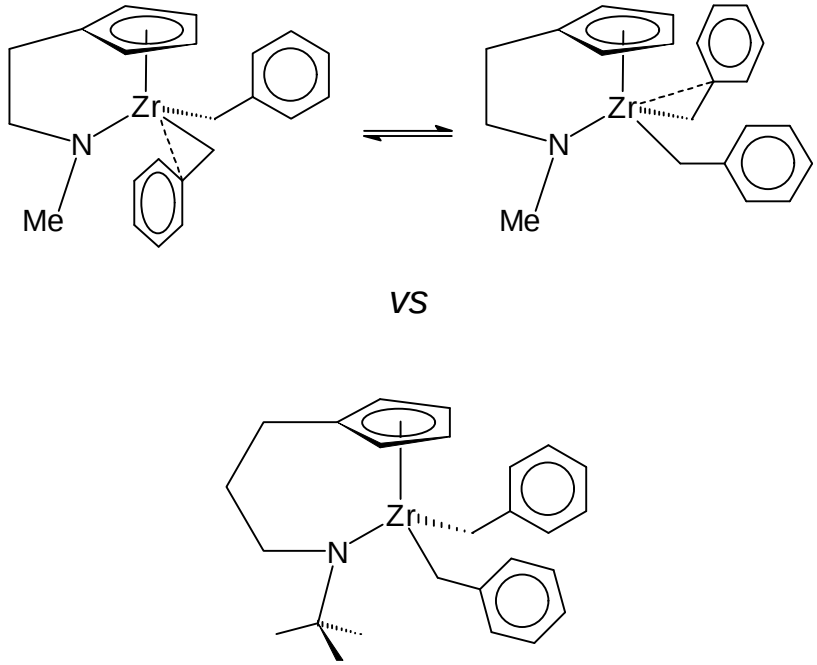
[a]) 300 MHz, C_6D_6, 25 °C.

For the sterically least congested complex, $[C_5H_4(CH_2)_2NMe]Zr(CH_2Ph)_2$ (**83**), the *o*-Ph protons show the largest upfield shift (6.47 ppm) and the benzylic carbon the highest $^1J_{CH}$ value (129.4 Hz) while the sterically most demanding complex $[C_5H_4(CH_2)_3N$-*t*-Bu]$Zr(CH_2Ph)_2$ (**89**) shows no upfield shift for the *o*-Ph protons (6.92 ppm) and the lowest $^1J_{CH}$ value (119.6 Hz) is observed for the benzylic carbon. An η^2-bonding mode for at least one of the benzyl ligands is suggested in $[C_5H_4(CH_2)_2NMe]Zr(CH_2Ph)_2$ (**83**) while for $[C_5H_4(CH_2)_3N$-*t*-Bu]$Zr(CH_2Ph)_2$ (**89**), the steric bulk of the ligand system seems too large and prevents η^2-bonding of the benzyl ligands. Although η^2-bonding of one of the benzyl ligands is likely in $[C_5H_4(CH_2)_2NMe]Zr(CH_2Ph)_2$ (**83**), both ^{1}H and ^{13}C NMR spectra have a symmetric appearance which may be due to the fast flipping of the benzyl groups (Scheme 5). This rearrangement could not be frozen out, low temperature ^{1}H and ^{13}C NMR spectra (toluene-d_8, -90 °C) showed the same symmetric resonances.

Table 5. ^{13}C-NMR data for $[C_5H_4(CH_2)_nNR]Zr(CH_2Ph)_2$[a]

comp.	Cp ipso	Cp CH		N-CH_2	-CH_2-	Cp-CH_2	$ZrCH_2$	R, α	R, β	Ph *ipso*	Ph *o*-CH	Ph *m*-CH	Ph *p*-CH
79	135.93	112.92	107.80	71.37		28.89	50.85	37.16		146.14	130.56	125.15	121.80
		(170.9)	(170.9)	(134.3)		(127.6)	(129.4)	(133.1)			(157.5)	(155.0)	(161.1)
80	135.83	113.06	108.64	59.98		29.39	50.34	44.95	21.23	146.53	130.32	125.59	121.85
		(170.9)	(170.9)	(130.0)		(127.6)	(128.2)	(120.9)	(125.7)		(157.5)	(153.8)	(162.4)
81	134.80	113.60	110.98	61.49		29.90	52.86	56.84	28.02	146.24	129.28	126.96	121.79
		(170.9)	(172.1)	(134.3)		(127.6)	(124.5)		(124.5)		(156.3)	(155.0)	(162.4)
82		110.5	110.1	55.5	26.6	29.8	50.2	34.3		145.4	121.8	129.6	126.4
83	122.69	110.64	110.31	39.66	26.77	30.11	49.61	50.72	14.89	145.66	129.51	126.30	121.82
		(170.9)	(170.9)	(127.6)	(125.7)	(126.4)	(127.6)	(132.5)	(126.6)		(157.5)	(153.8)	(162.0)
84	122.63	111.43	110.75	43.49	27.06	30.84	50.98	42.07	21.59	146.51	129.39	126.53	121.77
		(170.9)	(169.7)	(132.5)	(127.0)	(126.4)	(125.1)	(114.8)	(126.1)		(157.5)	(153.8)	(162.4)
85	126.60	114.83	112.55	48.22	28.02	34.14	63.53	57.08	29.65	149.04	128.74	126.66	121.45
		(172.1)	(169.7)	(132.5)	(127.0)	(126.4)	(119.6)		(124.9)		(156.3)	(153.8)	(157.5)

[a]) 75.4 MHz, C_6D_6, 25 ^{o}C, $^{1}J_{CH}$ coupling constants (Hz) in brackets.

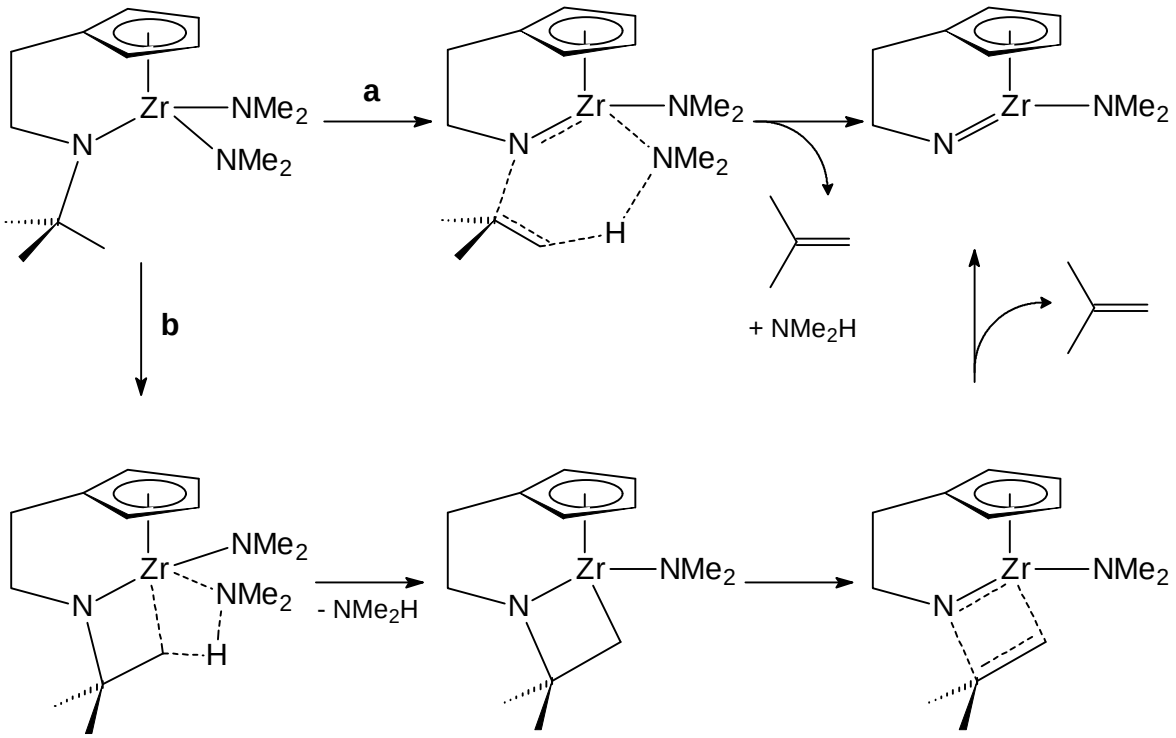


Scheme 5.

5.6 Thermolysis of $[C_5H_4(CH_2)_nN$-*t*-Bu$]Zr(NMe_2)_2$, Ligand Activation.

Intramolecular proteolysis by the amine function in $[C_5H_4(CH_2)_3N(H)$-*t*-Bu$]Zr(NMe_2)_3$ (**68**) was studied in detail. When a benzene-d_6 solution of this compound was heated, the reaction was complete in 80 hours at 120 ^oC giving a dark brown solution.[19] ^1H NMR spectroscopy and GC-MS analysis of the volatiles generated, revealed the presence of *iso*-butene and Me_2NH. The ^1H NMR spectrum of the product mixture formed showed broad signals at 7-5 ppm and 3-2 ppm. Heating of $[C_5H_4(CH_2)_2N$-*t*-Bu$]Zr(NMe_2)_2$ (**65**) in benzene-d_6 at 200 ^oC for 24 h resulted in complete decomposition and formation of Me_2NH and *iso*-butene[20] and the ^1H NMR spectrum showed the same broad resonances as observed for the thermolysis of $[C_5H_4(CH_2)_3N(H)$-t-Bu$]Zr(NMe_2)_3$ (**67**). Töpler pump determination of the volatile products of the thermolysis of $[C_5H_4(CH_2)_2N$-t-Bu$]Zr(NMe_2)_2$ (**65**) in benzene-d_6 gave 0.92-0.95 mol *iso*-butene/mol Zr and 1.1-1.33 mol Me_2NH/mol Zr. The formation of *iso*-butene and Me_2NH indicates activation of the *t*-Bu group. A plausible explanation *i.e.* transfer of the hydrogen from the *t*-Bu fragment to the dimethylamido group followed by extrusion of *iso*-butene is given in Scheme 6. Two possible mechanisms are displayed: one with a six membered transition state in which dimethylamine and *iso*-butene are formed in one step (**a**) and a two step mechanism featuring four center transition states (**b**). Group 4 metal complexes

bearing a terminal imido ligand are rare and are prone to give dimers or higher aggregates. Possibly, oligomers of the imido complex are formed.



Scheme 6.

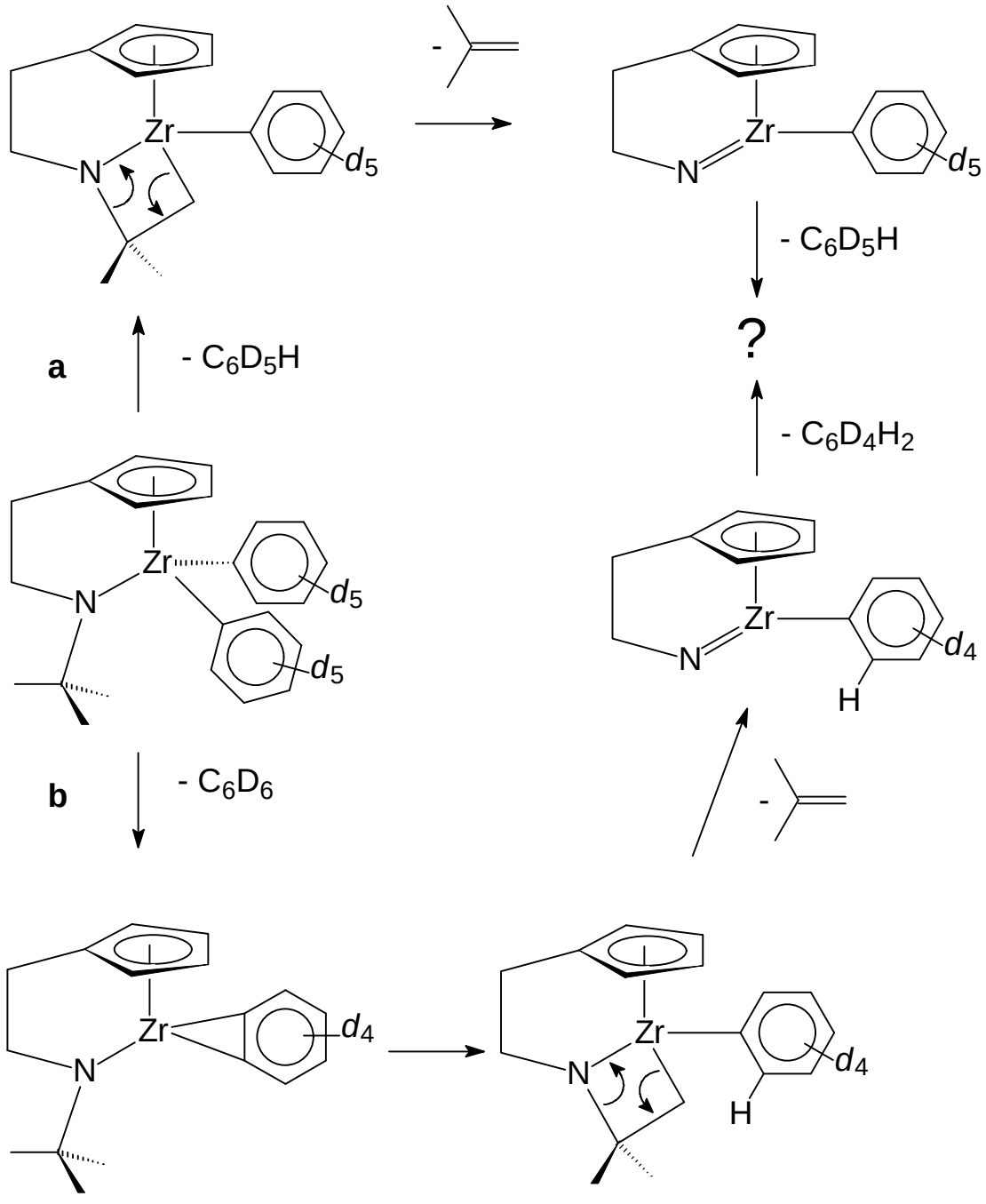
5.7 Thermolysis of Cp amido zirconium bis(carbyl) complexes $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrR_2$.

Zirconium bis(carbyl) complexes are known sources for aryne[21,22] and carbene complexes.[23] The bis(alkyl) titanium complexes $[C_5H_4(CH_2)_2N$-*t*-Bu$]TiR_2$ reported earlier in this thesis are useful precursors for aryne, olefin and alkylidene complexes (Chapter 3). Since we have a variety of Cp-amido zirconium bis(alkyl) compounds available it seems worthwile to study whether these can produce the corresponding aryne, olefin and alkylidene species. However, a preliminary investigation was discouraging: when a sample of $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrPh_2$ (**82**) in the presence of an excess of PMe_3 was heated (methylcyclohexane-d_{14}, 105 ^oC), formation of benzene and *iso*-butene was observed and the nearly colorless

solution turned dark brown. ^{1}H NMR showed in addition to the resonances of benzene and *iso*-butene broad resonances at 7-5 and 4-1 ppm and part of the product had precipitated. The species formed could not be identified. Thermolysis of the bis(methyl), bis(neopentyl) and bis(benzyl) complexes (**78**, **80** and **85**) proceeded in a similar way: *iso*-butene and RH had been formed together with unidentified products.

The thermolysis of $[C_5H_4(CH_2)_2N$-*t*-Bu]$ZrPh_2$ (**82**) was studied in more detail. Attempts to trap the possibly formed benzyne intermediate with diphenylacetylene failed, formation of *iso*-butene was observed instead and the amount of diphenylacetylene remained unchanged. When the deuterated species $[C_5H_4(CH_2)_2N$-*t*-Bu]$Zr(Ph$-$d_5)_2$ (**82-*d*$_{10}$**) was heated under the same conditions described above, the decomposition occurred at nearly the same rate ($k_H/k_D \approx 1.1$) and ^{1}H NMR spectra showed besides *iso*-butene, protonated benzenes. GC-MS analysis revealed formation of C_6D_6, C_6D_5H and $C_6D_4H_2$ in a approximately 1 : 4 : 1 ratio. The ^{1}H NMR spectra showed in addition that two equivalents of RH had been generated.

The liberation of C_6D_6, C_6D_5H and $C_6D_4H_2$ implies that at least two mechanisms are active (Scheme 7). [24] The formation of C_6D_5H and *iso*-butene and the k_H/k_D being close to unity suggest a mechanism in which the *t*–Bu amido fragment becomes directly activated giving C_6D_5H and the azazirconacyclobutane intermediate. This intermediate looses *iso*-butene generating an imido species which decomposes further under evolution of another C_6D_5H molecule (Scheme 7a). The evolution of C_6D_6 and $C_6D_4H_2$ suggests a second mechanism in which a benzyne species and C_6D_6 are generated followed by intramolecular C-H activation and liberation of *iso*-butene. Decomposition of the imido species would result in the evolution of $C_6D_4H_2$ (scheme 7b).



Scheme 7.

Transformation of the *t*-Bu amido group into an imido function, with loss of an organic fragment, has precedents. Direct R-transfer from an amido group has been observed by Green *et al.* for R = $SiMe_3$[25] and by Wolczanski *et al.* for R = H.[26] C-H activation is known for some bis(trimethylsilyl)amido compounds of group IV and V metals and actinides in the presence of hydride, alkyl or amido groups on the metal, giving silylazametallacyclobutanes under elimination of H_2, alkanes or amines.[27] A similar reaction producing an

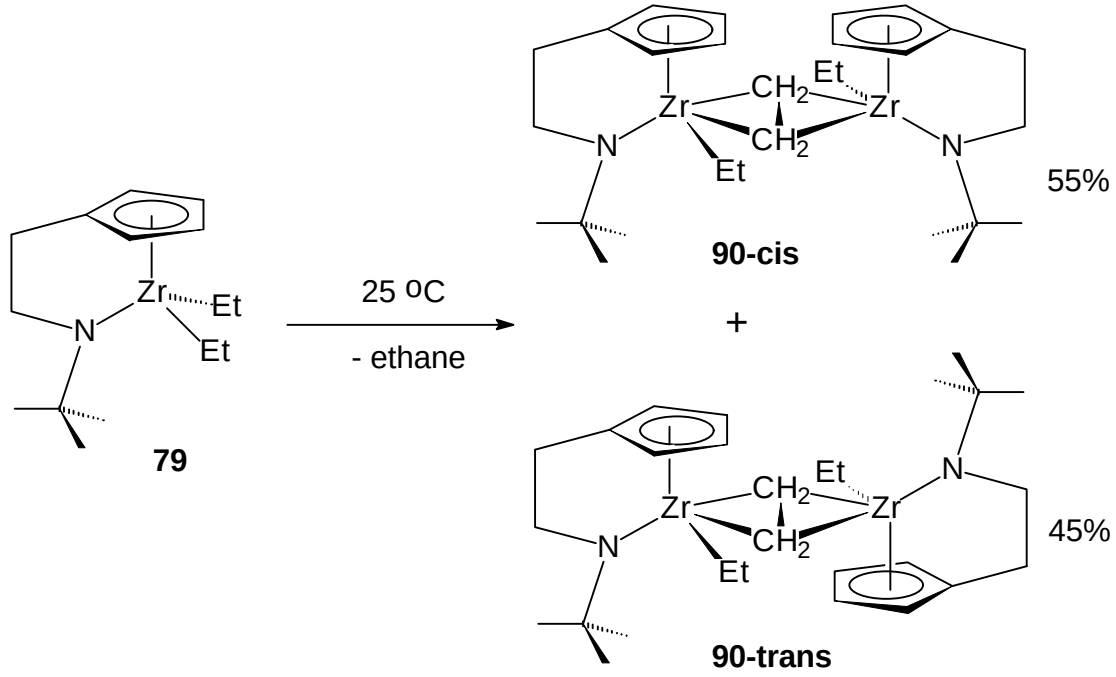
azametallacycle, is observed for (*t*-$Bu_3SiNH)_3ZrCH_3$. Solid state thermolysis resulted in the formation of a silylazametallacyclopentane and methane.[28] Liberation of *iso*-butene is known for complexes bearing the *tert*-butoxysilyl(*tert*-butyl)amido ligands[29] but it has not been reported for complexes with the [$C_5Me_4SiMe_2N$-*t*-Bu] ligand. Instead activation of the tetramethylcyclopentadienyl ligand has been observed.[30]

5.8 Thermolysis of [$C_5H_4(CH_2)_2$N-*t*-Bu]$ZrEt_2$ (79). Formation of the Ethene Bridged Dimer {[$C_5H_4(CH_2)_2$N-*t*-Bu]ZrEt}$_2$(μ:η^2,η^2-C_2H_4).

The decomposition of [$C_5H_4(CH_2)_2$N-*t*-Bu]$ZrEt_2$ (25 ^oC, C_6D_6, ^1H NMR) was complete in 7 h. The ^1H NMR spectrum of the formed product showed 6 resonances in the Cp region (6.19, 6.15, 5.87, 5.72, 5.40 and 5.17 ppm, an ABCD spin system at 3.8-2.4 ppm, a well resolved triplet at 1.72 ppm (J_{HH} = 7.88 Hz) coupled with a multiplet at 1-0.8 ppm. A sharp singlet at 0.78 ppm was assigned to ethane being formed during the thermolysis. Three high-field resonances were observed, a high order multiplet at 0.47 ppm which couples with another at -0.50 ppm and a singlet at -0.04 ppm which shows no coupling with the other two high field resonances. Two singlets at 1.10 and 1.05 ppm (integrating in 45:55 ratio), assigned to *t*-Bu groups, revealed the formation of two different compounds.

A white product was obtained when performing the reaction on a preparative scale and this was on the basis of ^1H and ^{13}C NMR spectroscopy identified as the ethene bridged dinuclear compound {[$C_5H_4(CH_2)_2$N-*t*-Bu]ZrEt}$_2$(μ:η^2,η^2-C_2H_4) (**90**). The resonances at 0.47, -0.49 (^1H) and 25.85 ($^1J_{CH}$ = 139.8 Hz) ppm (^{13}C) are assigned to the bridged ethene and from this the isolated complex was identified as the *cis* isomer of {[$C_5H_4(CH_2)_2$N-*t*-Bu]ZrEt}$_2$(μ:η^2,η^2-C_2H_4) (**90-*cis***) in which the *t*-Bu groups of the two {[$C_5H_4(CH_2)_2$N-*t*-Bu]ZrEt} moieties are directed to the same side (Scheme 8). The other compound mentioned in the thermolysis of [$C_5H_4(CH_2)_2$N-*t*-Bu]$ZrEt_2$ showed one single resonance (-0.04 ppm) for the bridged ethene and was identified as the *trans* isomer **90-*trans***.

The NMR data of **90-*cis*** and **90-*trans*** closely resemble those of a similar scandium complex {[$C_5Me_4SiMe_2$N-*t*-Bu]$ScPMe_3$}$_2$(μ:η^2,η^2-C_2H_4) (^1H NMR: 0.18, -0.54 ppm; ^{13}C NMR: 35.2 ppm, $^1J_{CH}$ = 142 Hz). The molecular structure of the complex showed it to be the *cis*-isomer.[31] Ethene bridged between two transition metals has been reported for the group 4 metals[32] and the formation of such complexes has been shown to be a significant polymerization catalyst deactivation mechanism.[33]



Scheme 8.

Like for the titanium bis(carbyl) complexes (Chapter 3), two thermolysis processes are recognized. At low temperature, a process in which only the carbyl ligands become activated, while at high temperature the Cp-amido ligand becomes involved in the thermolysis. The $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrR_2$ complexes are thermally more stable than their titanium analogues, very much in the way that Cp_2ZrR_2 compounds are more stable than Cp_2TiR_2. The $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrR_2$ compounds all decompose in a similar way (except the diethyl complex **79**) at 100 °C, or higher, giving RH, *iso*-butene and unidentified organometallic products.

Apparently, the activation energy for the carbyl ligand extrusion is so high that another thermolysis mechanism starts to compete *e.g.* the activation of the amido group. That zirconium complexes are, compared to titanium, less easily reduced may be an other reason since aryne, alkylidene and olefin complexes can be regarded as having resonance structures in which the metal center is divalent. Like for the corresponding titanium complexes, the studies on the thermolysis of $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrR_2$ complexes indicate that the $[C_5H_4(CH_2)_2N$-*t*-Bu] ligand can be considered as an inert spectator ligand at temperatures below 100 °C.

5.9 Concluding Remarks.

A facile synthesis route for a range of zirconium dichloro complexes $[C_5H_4(CH_2)_nNR]ZrCl_2$ has been developed. The dichlorides can be obtained in large quantities, in a relatively short time. However, it was not possible to synthesize $[C_5H_4(CH_2)_2NMe]ZrCl_2$.

Two routes to the bis(carbyl) complexes $[C_5H_4(CH_2)_nNR]ZrR'_2$ have been used: salt metathesis starting from the Cp-amido zirconium dichlorides $[C_5H_4(CH_2)_nNR]ZrCl_2$ and proteolysis of tetra(alkyl) zirconium by neutral $C_5H_5(CH_2)_nN(H)R$ ligands. The salt metathesis route is the most conveniently one, making a wide range of $[C_5H_4(CH_2)_nNR]ZrR'_2$ complexes accessible but in some cases proteolysis of tetra(alkyl) zirconium complexes offers relief when the related Cp-amido zirconium dichloro compound is not available as precursor, for example in the case of $[C_5H_4(CH_2)_2NMe]ZrCl_2$.

The bis(carbyl) complexes $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrR_2$ are more stable than the titanium analogues and except the diethyl compound $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrEt_2$, all bis(carbyl) complexes are fairly stable in solution up to 100 ^oC.

Thermolysis of the $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrR_2$ complexes proceeds by two processes: Selective activation of the carbyl ligands proceeds at low temperature as is found for $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrEt_2$ yielding the dinuclear complex $\{[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrEt\}_2(\mu{:}\eta^2,\eta^2$-$C_2H_4)$ (**90**). At high temperature (> 100 ^oC) direct activation of the *tert*-butyl amido moiety competes with the activation of the carbyl ligands.

C-H activation processes are not limited to bis(carbyl) complexes. The *t*-Bu ligand activation is also observed during the formation of $[C_5H_4(CH_2)_3N$-*t*-Bu$]Zr(NMe_2)_2$ by amine elimination. Even $[C_5H_4(CH_2)_2N$-*t*-Bu$]Zr(NMe_2)_2$ is affected in this way although at considerably higher temperature.

5.10 Experimental.

For general information see Chapter 2.

Synthesis of $Zr(NMe_2)_2Cl_2(THF)_2$ (63). To a solution of 5.1 g (19.0 mmol) $ZrCl_4$ in 50 mL of THF, 4.4 g (18.9 mmol) of $Zr(NMe_2)_4$ was added. Subsequently the clear yellow mixture was stirred for 16 h at room temperature. The reaction mixture was filtered and concentrated. Pentane was allowed to condense onto the solution overnight. Clear yellow crystals precipitated and were isolated. Yield: 9.0 g (22.7 mmol; 60%). ^1H NMR (200 MHz, C_6D_6): δ 3.78 (t, 8H, THF); 3.23 (s, 12H, NMe_2); 1.28 (q, 8H,

THF). Anal. Calcd for $C_{12}H_{28}N_2O_2Cl_2Zr$: C, 36.54; H, 7.15; Zr, 23.12. Found: C, 35.95; H, 6.86; Zr, 23.12.

Synthesis of [C$_5$H$_4$(CH$_2$)$_2$NMe]Zr(NMe$_2$)$_2$ (64). To a solution of 1.94 g (7.25 mmol) of $Zr(NMe_2)_4$ in 10 mL of toluene, 1.0 g (8.12 mmol) of $C_5H_5(CH_2)_2N(H)Me$ was added. The solution turned immediately light yellow. It was stirred at room temperature for an additional 2 h. The toluene was removed in vacuum and the remaining oily residue taken up in 10 mL of pentane. After removal of the pentane an oily product was vacuum transferred (150 ^oC and 0.01 torr) as an almost colorless oil. Yield: 1.57 g (5.22 mmol, 72%) $C_5H_4(CH_2)_2NMeZr(NMe_2)_2$. ^1H NMR (200 MHz, C_6D_6): 5.94 (t, 2H, $^3J_{HH}$ = 2.6 Hz, C_5H_4); 5.79 (t, 2H, $^3J_{HH}$ = 2.6 Hz, C_5H_4); 3.68 (t, 2H, $^3J_{HH}$ = 6.7 Hz, NCH_2); 3.04 (s, 3H, NMe); 2.89 (s, 12H, 2 x NMe2); 2.69 (t, 2H, $^3J_{HH}$ = 6.7 Hz, $C_5H_4\underline{CH_2}$). C NMR (50 MHz, C_6H_6): 136.4 (s, C_5H_4-*ipso*); 112.3 (d, $^1J_{CH}$ = 168.3 Hz, C_5H_4); 106.8 (d, $^1J_{CH}$ = 169.6, C_5H_4); 71.5 (t, $^1J_{CH}$ = 132.3 Hz, NCH_2); 43.9 (q, $^1J_{CH}$ = 131.2 Hz, NMe_2); 41.5 (q, $^1J_{CH}$ = 128.7 Hz, NMe); 29.5 (t, $^1J_{CH}$ = 126.4 Hz, $C_5H_4\underline{CH_2}$)

Synthesis of [C$_5$H$_4$(CH$_2$)$_2$N-t-Bu]Zr(NMe$_2$)$_2$ (65). To a solution of 2.56 g (9.57 mmol) of $Zr(NMe_2)_4$ in 15 mL of toluene, 1.6 g (9.7 mmol) of $C_5H_5(CH_2)_2N(H)$-t-Bu was added. The solution turned immediately yellow. After stirring overnight at 50 ^oC, the toluene was removed in vacuum and the orange oily residue was taken up in 20 mL of pentane and transferred to a distillation apparatus. After removal of the pentane, the remaining brown oil was vacuum transferred (120-130 ^oC and 0.001 torr) to give a light green oil. Yield: 2.7 (7.9 mmol, 81%) $[C_5H_4(CH_2)_2N$-t-Bu$]Zr(NMe_2)_2$. ^1H NMR (200 MHz, C_6D_6): δ 5.90 (t, J_{HH} = 2.4 Hz, 2H C_5H_4); 5.86 (t, J_{HH} = 2.4 Hz, 2H, C_5H_4); 3.63 (t, $^3J_{HH}$ = 6.4 Hz, 2H, NCH_2); 2.81 (s, 12H, 2 x NMe_2); 2.58 (t, $^3J_{HH}$ = 6.4 Hz, 2H, $C_5H_4C\mathit{H_2}$); 1.24 (s, 9H, *t*-Bu). ^{13}C NMR (50 MHz, C_6D_6): δ 135.2 (s, C_5H_4-*ipso*); 111.5 (d, $^1J_{CH}$ = 157.2 Hz, C_5H_4); 107.9 (d, $^1J_{CH}$ = 162.9 Hz, C_5H_4); 60.5 (t, $^1J_{CH}$ = 132.9 Hz, NCH_2); 57.0 (s, $\underline{C}Me_3$); 44.5 (q, $^1J_{CH}$ = 138.7 Hz, NMe_2); 31.1 (t^1J_{CH} = 128.7 Hz, $C_5H_4\underline{CH_2}$); 30.0 (q, $^1J_{CH}$ = 124.1 Hz, $C\underline{Me_3}$). Anal. Calcd for $C_{15}H_{29}N_3Zr$: C, 52.58; H, 8.53; Zr, 26.62. Found: C, 52.51; H, 8.65; Zr, 26.56.

Synthesis of [C$_5$H$_4$(CH$_2$)$_3$N(H)-t-Bu]Zr(NMe$_2$)$_3$ (67). To a solution of 3.07 g (11.5 mmol) of $Zr(NMe_2)_4$ in 20 mL of toluene, 2.3 g (12.8 mmol) of $C_5H_5(CH_2)_3N(H)$-*t*-Bu was added. The solution turned light green. The mixture was stirred for 2 h at room temperature. The toluene was pumped off and the oily residue was stripped twice with 15 mL of pentane. The volatiles were removed in high vacuum (0.001 torr). The oil was not purified further. ^1H NMR (C_6D_6) revealed the presence of some free ligand (5%). ^1H NMR (200 MHz, C_6D_6): δ 6.00 (m, J_{HH} = 2.4 Hz, 2H, C_5H_4); 5.95 (m, J_{HH} = 2.4 Hz, 2H, C_5H_4); 2.94 (s, 18H, 3 x NMe_2); 2.61 (t, $^3J_{HH}$ = 7.7 Hz, 2H, $C_5H_4\underline{CH_2}$); 2.50 (q, $^3J_{HH}$ = 7.7 Hz, 2H, NCH_2); 1.66 (quint, $^3J_{HH}$ = 7.7 Hz, 2H, $NCH_2\underline{CH_2}$); 1.01 (s, 9H, *t*-Bu); 0.25 (s, 1H, NH).

Synthesis of [C$_5$H$_4$(CH$_2$)$_3$NAd]Zr(NMe$_2$)$_2$ (69). A solution of 2.00 g (7.48 mmol) of $Zr(NMe_2)_2$ and 1.90 g (7.44 mmol) of $C_5H_5(CH_2)_3N(H)$Ad in 50 mL of toluene was refluxed for 12 h. The toluene was removed in vacuum and the light brown residue was stripped with 20 mL of pentane. The residue was

extracted with 20 mL pentane and filtered. The solution was concentrated to 10 mL and slowly cooled to -90 °C. Light brown crystals formed. Yield: 1.50 g (3.45 mmol, 46%) of $[C_5H_4(CH_2)_3NAd]Zr(NMe_2)_2$. ^{1}H NMR (300 MHz, C_6D_6): δ 6.19 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 5.83 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 3.01 (m, 2H, $C_5H_4\underline{CH_2}$); 2.98 (s, 12H, NMe_2); 2.59 (m, 2H, NCH_2); 2.06 (m, 3H, C-CH-C of adamantyl) 1.65 (m, 12H, C-CH_2-C of adamantyl); 1.61 (m, 2H, $NCH_2\underline{CH_2}$).

Synthesis of Zr[C$_5$H$_4$(CH$_2$)$_2$N-i-Pr]Cl$_2$. (70). To a solution of 2.1 g (5.3 mmol) of $Zr(NMe_2)_2Cl_2\cdot(THF)_2$ in 50 mL of toluene, 0.8 mL (5.3 mmol) of $C_5H_5(CH_2)_2N(H)$-*i*-Pr was added. The reaction mixture was stirred for 18 h at 75 ºC. The yellow solution was filtered and the volatiles were removed in vacuum giving a yellow solid which was stripped with 10 mL of pentane and washed 3 times with 25 mL of pentane. The resulting light yellow solid was dried in vacuum and was identified as the dimethylamine adduct (^{1}H, ^{13}C NMR). After sublimation (0.05 torr, 60 ºC) the amine-free compound was isolated as an off white solid. Yield: 1.2 g (3.9 mmol; 74%). ^{1}H NMR (200 MHz, C_6D_6): δ 5.81 (t, 2H, C_5H_4); 5.74 (t 2H, C_5H_4); 4.55 (m, 1H, $\underline{CH}Me_2$); 3.48 (t, 2H, CH_2N); 2.31 (t, 2H, $C_5H_4\underline{CH_2}$); 0.89 (d, 6H, $CH\underline{Me_2}$. ^{13}C NMR (50.3 MHz, C_6D_6): δ 141.8 (s, C_5H_4-*ipso*); 115.5 (d, $^1J_{CH}$ = 172.1 Hz, C_5H_4); 111.8 (d, $^1J_{CH}$ = 173.4 Hz, C_5H_4); 63.3 (t, $^1J_{CH}$ = 134.3 Hz, NCH_2); 49.4 (d, $^1J_{CH}$ = 129.4 Hz, $\underline{C}HMe_2$); 28.6 (t, $^1J_{CH}$ = 113.2 Hz, $C_5H_4\underline{CH_2}$); 19.5 (q, $^1J_{CH}$ = 127.8 Hz, $CH\underline{Me_2}$). IR (cm^{-1}): 3079 (sh), 1378 (s), 1358 (sh), 1342 (sh), 1183 (sh), 1168 (sh), 1159 (s), 1059 (m), 1042 (m), 1024 (m), 991 (s), 885 (m), 826 (sh), 815 (s), 723 (m), 609 (w), 525 (m), 469 (m), 427 (m). Anal. Calcd for $C_{10}H_{15}NCl_2Zr$:: C, 38.58; H, 4.86; Zr, 29.30. Found: C, 38.58; H, 4.81; Zr, 29.20. Mol. weight Calcd for $C_{10}H_{15}NCl_2Zr$: 311.4 g/mol. Found: 350.9 ± 30 g/mol.

Synthesis of Zr[C$_5$H$_4$(CH$_2$)$_2$N-t-Bu]Cl$_2$ (71). To a clear yellow solution of 4.6 g (12.2 mmol) of $Zr(NMe_2)_2Cl_2\cdot(THF)_2$ in 50 mL of toluene, 2.2 mL (12.4 mmol) of $C_5H_5(CH_2)_2N(H)$-*t*-Bu was added. The reaction mixture was stirred for 18 h at 75 ºC. The orange-yellow solution was filtered and the volatiles were removed under vacuum. The orange solid was stripped with 15 mL of pentane and washed 3 times with 25 mL of pentane. The yellow crystals were characterized as the dimethylamine adduct. After sublimation (0.05 torr, 60 ºC) the amine-free compound was isolated as a cream white solid. Yield: 3.1 g (8.4 mmol; 69%). ^{1}H NMR (200 MHz, C_6D_6): δ 5.99 (t, 2H, C_5H_4); 5.79 (t 2H, C_5H_4); 3.47 (t, 2H, CH_2N); 2.23 (t, 2H, $C_5H_4\underline{CH_2}$); 1.25 (d, 9H, t-Bu). ^{13}C NMR (50.3 MHz, C_6D_6): δ 141.4 (s, C_5H_4-*ipso*); 115.7 (d, $^1J_{CH}$= 106.2 Hz, C_5H_4); 113.3 (d, $^1J_{CH}$ = 112.3 Hz, C_5H_4); 64.9 (t, $^1J_{CH}$ = 136.1 Hz, NCH_2); 57.2 (s, $\underline{C}Me_3$); 29.3 (t, $^1J_{CH}$ = 129.4 Hz, $C_5H_4\underline{CH_2}$); 27.7 (q, $^1J_{CH}$ = 125.3 Hz, $C\underline{Me_3}$). IR (cm^{-1}): 3077 (sh), 2726 (w), 2679 (w), 1377 (sh), 1365 (sh), 1346 (sh), 1307 (w), 1247 (m), 1199 (w), 1168 (m), 1086 (w), 980 (w), 951 (w), 888 (w), 817 (m), 768 (m), 722 (m), 557 (w), 535 (w), 487 (w). Anal. Calcd for $C_{11}H_{17}NCl_2Zr$: C, 40.60; H, 5.27; Zr, 28.03. Found: C, 40.55; H, 5.27; Zr, 28.13. Mol. weight Calcd for $C_{11}H_{17}NCl_2Zr$: 325.4 g/mol. Found: 332.3 ± 25 g/mol.

Synthesis of [C$_5$H$_4$(CH$_2$)$_3$NMe]ZrCl$_2$.HNMe$_2$ (72). A solution (0 °C) of 6.76 g (25.27 mmol) of $Zr(NMe_2)_4$ in 30 mL of toluene was treated with 3.4 g (24.8 mmol) of $C_5H_5(CH_2)_3N(H)Me$ and stirred for 0.5 h at 50 °C. The resulting light green-yellow solution was cooled to 0 °C and 6.4 mL (50.4

mmol) of Me_3SiCl was added. A light yellow precipitate formed which dissolved upon heating to reflux. After refluxing for 4 h a clear yellow brown solution had been formed. The solvent was removed in vacuum and the residue was washed twice with 30 mL of pentane. After drying in vacuum, the residue was extracted with 60 mL of hot toluene. Concentrating at 80-90 ^oC to 15 mL and slowly cooling to -20 ^oC gave cream colored crystals of $[C_5H_4(CH_2)_3NMe]ZrCl_2.HNMe_2$. Yield: 6.48 g (18.92 mmol, 75%). ^1H NMR (200 MHz, $CDCl_3$): δ 6.20 (m, J_{HH} = 2.68 Hz, 2H, C_5H_4); 6.07 (m, J_{HH} = 2.68 Hz, 2H, C_5H_4); 2.99 (s, 3H, NMe); 2.93 (m, 2H, NCH_2); 2.75 (m, 2H, $C_5H_4\underline{CH_2}$); 2.62 (d, $^3J_{HH}$ = 5.86 Hz, 6H, $HN\underline{Me_2}$); 2.12 (m, 2H, $NCH_2\underline{CH_2}$). Sublimation of 0.95 g of $[C_5H_4(CH_2)_3NMe]ZrCl_2.HNMe_2$ at 150-160 ^oC and 10^{-3} torr yielded 0.75 g (91%) of $[C_5H_4(CH_2)_3NMe]ZrCl_2$ (**73**). ^1H NMR (300 MHz, $CDCl_3$): δ 6.46 (m, J_{HH} = 2.75 Hz, 2H, C_5H_4); 6.05 (m, J_{HH} = 2.57 Hz, 2H, C_5H_4); 3.27 (s, 3H, NMe); 2.95 (m, 2H, NCH_2); 2.80 (m, 2H, $C_5H_4\underline{CH_2}$); 2.17 (m, 2H, $NCH_2\underline{CH_2}$). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 127.64 (s, C_5H_4-*ipso*); 114.17 (d, $^1J_{CH}$ = 174.6 Hz, C_5H_4); 112.31 (d, $^1J_{CH}$ = 172.1 Hz, C_5H_4); 55.85 (t, $^1J_{CH}$ = 134.9 Hz, NCH_2); 37.24 (q, $^1J_{CH}$ = 135.5 Hz, NMe); 28.95 (t, $^1J_{CH}$ = 127.0 Hz, $C_5H_4\underline{CH_2}$); 26.01 (t, $^1J_{CH}$ = 128.2 Hz, $NCH_2\underline{CH_2}$). IR (cm^{-1}): 3102 (m), 3084 (m), 2741 (m), 1800 (w), 1759 (w), 1715 (w), 1670 (w), 1620 (w), 1530 (w), 1497 (m), 1481 (m), 1447 (m), 1433 (m), 1420 (m), 1393 (m), 1333 (m), 1273 (m), 1254 (s), 1231 (w), 1188 (s), 1163 (m), 1121 (s), 1074 (w), 1063 (w), 1042 (s), 1034 (s), 984 (m), 932 (s), 901 (s), 880 (m), 860 (m), 839 (m), 810 (vs), 748 (vw), 729 (vw), 683 (w), 667 (w), 56 (w), 638 (w), 621 (w), 608 (w), 577 (w), 559 (w), 530 (s), 511 (m), 484 (w), 469 (w), 453 (w), 438 (w).

Synthesis of $[C_5H_4(CH_2)_3NEt]ZrCl_2$ (74). To a cooled (0 ^oC) solution of 6.11 g (22.8 mmol) of $Zr(NMe_2)_4$ in 50 mL of toluene, 3.8 g (25 mmol) of $C_5H_5(CH_2)_3N(H)Et$ was added. The solution became light yellow-green upon warming and after refluxing for 15 min the mixture was cooled to 0 ^oC and 5.8 mL (46 mmol) of Me_3SiCl was added while stirring at room temperature for 20 min. the solution became turbid. Refluxing for 10 min. gave a clear deep yellow solution which was filtered and concentrated to 15 mL at reflux. Slowly cooling to 0 ^oC afforded light orange crystals which were washed with 20 mL of pentane. Yield 4.72 g (15.1 mmol, 66%). A pure sample was obtained by sublimation (150-160 ^oC and 10^{-3} torr). ^1H NMR (300 MHz, $CDCl_2$): δ 6.52 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 6.02 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 3.81 (q, $^3J_{HH}$ = 6.47 Hz, 2H, $N\underline{CH_2}CH_3$); 2.92 (m, 2H, NCH_2); 2.81 (m, 2H, $C_5H_4\underline{CH_2}$); 2.15 (m, 2H, $NCH_2\underline{CH_2}$); 1.21 (t, $^3J_{HH}$ = 6.47 Hz, 3H, $NCH_2\underline{CH_3}$). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 128.03 (s, C_5H_4-*ipso*); 114.48 (d, $^1J_{CH}$ = 174.6 Hz, C_5H_4); 112.20 (d, $^1J_{CH}$ = 17.1 Hz, C_5H_4); 51.27 (t, $^1J_{CH}$ = 134.9 Hz, NCH_2); 42.93 (t, $^1J_{CH}$ = 130.6 Hz, $N\underline{CH_2}CH_3$); 29.83 (t, $^1J_{CH}$ = 127.0 Hz, $C_5H_4\underline{CH_2}$); 26.31 (t, $^1J_{CH}$ = 128.2 Hz, $NCH_2\underline{CH_2}$); 12.69 (q, $^1J_{CH}$ = 127.4 Hz, $NCH_2\underline{CH_3}$). IR (cm^{-1}): 3102 (m), 3086 (w), 2805 (m), 2701 (m), 2645 (w), 1807 (w), 1767 (m), 1717 (m), 1694 (w), 1682 (w), 1624 (m), 1495 (m), 1437 (m), 1397 (vw), 1339 (s), 1289 (s), 1269 m), 1242 (m), 1227 (s), 1177 (s), 1161 (s), 1113 (s), 1082 (m), 1057 (s), 1040 (s), 1007 (s), 943 (m), 930 (m), 903 (w), 878 (m), 862 (s), 843 (w), 810 (vs), 779 (s), 737 (w), 654 (w) 610 (w), 563 (s), 525 (m) 421 (s), 409 (s).

Synthesis of $Zr[C_5H_4(CH_2)_3N$-i-Pr$]Cl_2$ (75). A solution of 3.9 g (9.9 mmol) of $Zr(NMe_2)_2Cl_2\cdot(THF)_2$ and 1.6 mL (9.9 mmol) of $C_5H_5(CH_2)_3N(H)$-*i*-Pr in 50 mL of toluene was heated for 24 h at 75 ^oC. After

work-up pale yellow crystals were isolated. Yield: 2.30 g (7.0 mmol; 71%). ^{1}H NMR (200 MHz, C_6D_6): δ 5.81 (t, 2H, C_5H_4); 5.74 (t, 2H, C_5H_4); 4.55 (m, 1H, $\underline{CH}Me_2$); 3.48 (t, 2H, NCH_2); 2.31 (t, 2H, $C_5H_4\underline{CH_2}$); 0.89 (d, 6H, $CH\underline{Me_2}$). ^{13}C NMR (50.3 MHz, C_6D_6); δ 114.9 (d, $^{1}J_{CH}$ = 173.4 Hz, C_5H_4); 111.9 (d, $^{1}J_{CH}$ = 174.6 Hz, C_5H_4); 46.5 (d, $^{1}J_{CH}$ = 117.2 Hz, $\underline{CH}Me_2$); 44.2 (t, $^{1}J_{CH}$ = 134.3 Hz, NCH_2); 30.5 (t, $^{1}J_{CH}$ = 127.6 Hz, $C_5H_4\underline{CH_2}$); 26.4 (t, $^{1}J_{CH}$ = 127.6 Hz, $NCH_2\underline{CH_2}$); 19.6 (q, $^{1}J_{CH}$ = 127.0 Hz, $CH\underline{Me_2}$). IR (cm^{-1}): 3106 (sh), 3088 (sh), 2683 (w), 2628 (m), 1769 (w), 1723 (w), 1714 (w), 1690 (w), 1681 (w), 1642 (w), 1627 (w), 1493 (w), 1357 (m), 1348 (m), 1242 (m), 1181 (m), 1171 (m), 1160 (m), 1106 (m), 1087 (m), 1072 (m), 1050 (m), 1033 (m), 866 (m), 813 (s), 802 (s), 609 (m), 597 (m), 456 (m), 442 (m), 417 (m). Anal. Calcd for $C_{11}H_{17}NCl_2Zr$: C, 40.60; H, 5.27; Zr, 28.03. Found: C, 40.66; H, 5.27; Zr, 28.05.

Synthesis of [$C_5H_4(CH_2)_3$N-t-Bu]$ZrCl_2$ (76). To a solution of 4.53 g (11.48 mmol) of $Zr(NMe_2)_2Cl_2(THF)_2$ in 50 mL of toluene, 2.2 mL (11.6 mmol) of $C_5H_5(CH_2)_3N(H)$-*t*-Bu was added and the mixture was stirred for 24 h at 90 °C. A pale green solution was obtained. After cooling to room temperature the solution was filtered and concentrated to about 20 mL. The product was precipitated by adding 80 mL of pentane yielding a cream colored power which was washed 2 times with 50 mL of pentane and dried in vacuum. According to the ^{1}H NMR spectrum coordinated Me_2NH was present together with some other unidentified products (about 15% of total integral). Sublimation (170-190 °C, 0.005 torr) of the crude product gave 2.31 g (6.83 mmol, 59%) white material. A ^{1}H NMR spectrum of the product showed it to be a 4:1 mixture of [$C_5H_4(CH_2)_3$N-*t*-Bu]$ZrCl_2$ (**76a**) and {[$C_5H_4(CH_2)_3$N-*t*-Bu]$ZrCl_2$}$_2$ (**76b**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.51 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4, **76a**); 6.27 (m, J_{HH} = 2.42 Hz, 4H, 2x C_5H_4, **76b**); 6.19 (m, J_{HH} = 2.42 Hz, 4H, 2x C_5H_4, **76b**); 6.12 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4, **76a**); 3.15 (m, 2H, $C_5H_4\underline{CH_2}$, **76a**); 2.73 (m, 2H, NCH_2, **76a**); 2.67 (t, $^{3}J_{HH}$ = 7.23 Hz, 4H, 2x NCH_2, **76b**); 2.55 (t, $^{3}J_{HH}$ = 7.41 Hz, 4H, 2x $C_5H_4\underline{CH_2}$, **76b**); 1.90 (m, 2H, $NCH_2\underline{CH_2}$, **76a**); 1.69 (quint, $^{3}J_{HH}$ = 7.34 Hz, 4H, 2x $NCH_2\underline{CH_2}$, **76b**); 1.55 (s, 9H, *t*-Bu, **76a**); 1.06 (s, 18H, 2x *t*-Bu, **76b**).

Synthesis of [$C_5H_4(CH_2)_3$NAd]$ZrCl_2$ (77). A solution of 1.25 g (2.88 mmol) of [$C_5H_4(CH_2)_3$NAd]$Zr(NMe_2)_2$ in 10 mL of toluene was treated with 0.73 mL (5.75 mmol) of Me_3SiCl and the mixture was stirred at 60 °C for 4 h. An off-white precipitate formed. After cooling to 0 °C 10 mL of pentane was added and the precipitate was allowed to settle. The solvents were removed by filtration and the gray residue was washed with pentane and dried in vacuum. Isolated: 0.91 g (2.18 mmol, 75%) of [$C_5H_4(CH_2)_3$NAd]$ZrCl_2$. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.47 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 6.12 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 3.15 (m, 2H, $C_5H_4\underline{CH_2}$); 2.70 (m, 2H, NCH_2); 2.18 (m, 9H, Overlapped resonances of C-CH_2-CH and C*H* of adamantyl); 1.85 (m, 2H, $NCH_2\underline{CH_2}$, 6H, CH-CH_2-CH of adamantyl). ^{13}C NMR (75.4 MHz, $CDCl_3$, 50 °C): 131.55 (s, C_5H_4-*ipso*); 116.76 (d, $^{1}J_{CH}$ = 175.8 Hz,C_5H_4); 114.90 (d, $^{1}J_{CH}$ = 173.4 Hz, C_5H_4); 60.30 (s, -C≡ adamantyl); 48.21 (t, $^{1}J_{CH}$ = 134.3 Hz, NCH_2); 40.73 (t, $^{1}J_{CH}$ = 124.5 Hz, CH_2, adamantyl); 37.61 (t, $^{1}J_{CH}$ = 128.0 Hz, $C_5H_4\underline{CH_2}$); 36.33 (t, $^{1}J_{CH}$

= 127.6 Hz, CH_2, adamantyl); 29.45 (d, $^1J_{CH}$ = 131.9 Hz, CH, adamantyl); 26.93 (t, $^1J_{CH}$ = 128.2 Hz, $NCH_2\underline{CH_2}$).

Thermolysis of [C₅H₄(CH₂)₂N-t-Bu]Zr(NMe₂)₂ (65) in C₆D₆. A solution of 89.3 mg (0.244 mmol) of $[C_5H_4(CH_2)_2N$-*t*-Bu$]Zr(NMe_2)_2$ in 0.5 mL of C_6D_6 was sealed in an NMR tube under vacuum. The NMR tube was kept in an oven at 210 °C for 36 hr. The decomposition was monitored by ^{1}H NMR spectroscopy at regular intervals. The ^{1}H NMR spectrum showed the formation of *iso*-butene and Me_2NH, After 24 h, all starting material had disappeared. At the vacuum line the NMR tube was broken under vacuum and all volatiles were condensed to a 0.100 N aqueous solution of HCl (1.665 mmol). The solution was warmed to room temperature and stirred for 30 min. to trap all amine. The solution was degassed using three freeze and thaw cycles at -30 °C and the gas was collected in a trap cooled to -196 °C. The trap was warmed to -30 °C and residual gas was pumped through a cold trap (-70 °C) in a calibrated volume using a Töpler pump. 0.224 mmol (0.92 mol/mol Zr) of *iso*-butane (MS) gas was collected. All condensed residues were transferred back to the aqueous solution. The solution was titrated with NaOH solution (1.340 mmol) yielding 1.33 mol Me_2NH/mol Zr. A second experiment was carried out with 121.6 mg (0.332 mmol) of $[C_5H_4(CH_2)_2N$-t-Bu$]Zr(NMe_2)_2$ yielding 0.315 mmol *iso*-butene (0.95 mol/mol Zr) and 0.365 mmol Me_2NH (1.1 mol/mol Zr).

Synthesis of [C₅H₄(CH₂)₂N-t-Bu]ZrMe₂ (78). A cooled (0 °C) suspension of 1.07 g (3.29 mmol) of $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrCl_2$ in 30 mL of ether was treated with 8 mL 0.88 M (7.0 mmol) of MeLi in ether. The mixture was stirred for 3 h at room temperature giving a nearly colorless solution and a white precipitate. After removal of the solvent in vacuum the sticky, off-white residue was stripped with 20 mL of pentane. The residue was extracted with 40 mL of pentane and filtered. Removal of the pentane in vacuum left a nearly colorless oil. Yield 0.82 g (2.88 mmol, 87%) of $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrMe_2$. ^{1}H NMR (300 MHz, C_6D_6): δ 6.03 (m, J_{HH} = 2.57 Hz, 2H, C_5H_4); 5.82 (m, J_{HH} = 2.57 Hz, 2H, C_5H_4); 3.44 (t, $^3J_{HH}$ = 6.41 Hz, 2H, NCH_2); 2.35 (t, $^3J_{HH}$ = 6.41 Hz, 2H, $C_5H_4\underline{CH_2}$); 1.39 (s, 9H, *t*-Bu); 0.03 (s, 6H, 2 x Me). ^{13}C NMR (75.4 MHz, C_6D_6): δ 133.11 (s, C_5H_4-*ipso*); 112.80 (d, $^1J_{CH}$ = 169.7 Hz, C_5H_4); 109.81 (d, $^1J_{CH}$ = 173.4 Hz, C_5H_4); 60.73 (t, $^1J_{CH}$ = 133.7 Hz, NCH_2); 55.43 (s, $N\underline{C}Me_3$); 31.43 (q, $^1J_{CH}$ = 113.5 Hz, Me); 29.75 (t, $^1J_{CH}$ = 128.2 Hz, $C_5H_4\underline{CH_2}$); 28.62 (q, $^1J_{CH}$ = 124.5 Hz, $NC\underline{Me_3}$). IR (cm^{-1}): 3086 (vw), 2760 (w), 2675 (w), 1667 (w), 1613 (w), 1466 (sh, nujol), 1358 (m), 1344 (vw), 1321 (w), 1246 (m), 1204 (s), 1125 (m), 1088 (s), 1040 (m), 1028 (w), 980 (m), 955 (m), 862 (m), 841 (m), 806 (vs), 766 (m), 681 (m) 644 (m), 557 (m), 527 (w), 461 (s).

Synthesis of [C₅H₄(CH₂)₂N-t-Bu]ZrEt₂ (79). A cooled (-10 °C) suspension of 0.46 g (1.41 mmol) of $[C_5H_4(CH_2)_2N$-*t*-Bu$]ZrCl_2$ in 30 mL of ether was treated with 2.0 mL 1.54 M of EtMgBr in ether. The mixture was stirred for 1.5 h at -10 °C giving a clear solution and a white precipitate. The work-up procedure was also performed at -10 °C. The solvent was removed in vacuum and the white oily residue was stripped with 20 mL of pentane. The residue was extracted with 50 mL of pentane and after filtration a clear nearly colorless solution was obtained. The solution was concentrated to 10 mL and transferred into a small vessel. Removal of the pentane in vacuum left a nearly colorless oil.

Yield: 0.38 g (1.22 mmol, 86%, based on $[C_5H_4(CH_2)_2N$-*t*-Bu]$ZrEt_2$). A ^1H NMR spectrum showed beside the resonances of the bis-ethyl complex also the appearance of the resonances of the decomposition products. ^1H NMR (300 MHz, C_6D_6): δ 5.94 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 5.86 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 3.42 (t, $^3J_{HH}$ = 6.41 Hz, 2H, NCH_2); 2.38 (t, $^3J_{HH}$ = 6.41 Hz, 2H, $C_5H_4CH_2$); 1.36 (t, $^3J_{HH}$ = 8.05 Hz, 6H, $CH_2\underline{CH_3}$); 1.33 (s, 9H, CMe_3); 0.69 (m, 2H, $\underline{CH_2}CH_3$); 0.44 (m, 2H, $\underline{CH_2}CH_3$).

Thermolysis of [C₅H₄(CH₂)₂N-t-Bu]ZrEt₂ (79). An NMR sample of **79** was monitored at 25 °C at regular times. Evolution of ethane (NMR) was observed and after 7 hours the bis ethyl complex had completely been converted into the *cis* and *trans* isomers of $\{[C_5H_4(CH_2)_2N$-*t*-Bu]ZrEt$\}_2(\mu{:}\eta^2,\eta^2\text{-}C_2H_4)$ (**90**) in a 1 to 0.86 ratio.

Synthesis of cis-{[C₅H₄(CH₂)₂N-t-Bu]ZrEt}₂(μ:η², η²-C₂H₄) (90-cis). To a cooled (-10 °C) suspension of 0.61 g (1.87 mmol) of $[C_5H_4(CH_2)_2N$-*t*-Bu]$ZrCl_2$ in 30 mL of ether, 2.5 mL 1.54 M (3.8 mmol) of EtMgBr in ether was added and the mixture was stirred for 2 h at -10 °C. After removal of the ether in vacuum the residue was stripped with 20 mL of pentane. The residue was extracted with 50 mL of pentane and filtered. The clear and nearly colorless solution was concentrated to 5 mL and stirred for 3 h at 30 °C. The solution turned orange and an off-white powder precipitated. The powder was isolated on a frit, washed twice with 5 mL of pentane and dried in vacuum. Yield: 0.075 g (0.13 mol, 14%) of $\{[C_5H_4(CH_2)_2N$-t-Bu]ZrEt$\}_2(\mu{:}\eta^2,\eta^2\text{-}C_2H_4)$ (**90**). An NMR sample showed it to be predominantly the *cis* isomer. ^1H NMR (300 MHz, THF-d_8): δ 6.27 (m, 2H, C_5H_4); 6.20 (m, 2H, C_5H_4); 5.75 (m, 2H, C_5H_4); 5.16 (m, 2H, C_5H_4); 3.86 (m, 2H, NCH_2); 3.64 (m, 2H, NCH_2); 2.76 (m, 2H, $C_5H_4\underline{CH_2}$); 2.65 (m, 2H, $C_5H_4\underline{CH_2}$); 1.35 (t, $^3J_{HH}$ = 7.51 Hz, 6H, $CH_2\underline{CH_3}$); 1.10 (s, 18H, *t*-Bu); 0.63 (m, 2H, $\underline{CH_2}CH_3$); 0.49 (m, 2H, $\underline{CH_2}CH_3$); 0.32 (m, 2H, C_2H_4); -0.67 (m, 2H, C_2H_4). ^{13}C NMR (75.4 MHz, d_8-THF): δ 135.27 (s, C_5H_4-*ipso*); 112.97 (d, $^1J_{CH}$ = 166.0 Hz, C_5H_4); 110.82 (d, $^1J_{CH}$ = 166.0 Hz, C_5H_4); 110.12 (d, $^1J_{CH}$ = 170.9 Hz, C_5H_4); 107.06 (d, $^1J_{CH}$ = 169.7 Hz, C_5H_4); 61.81 (t, $^1J_{CH}$ = 133.1 Hz, NCH_2); 57.69 (s, $\underline{C}Me_3$); 33.18 (t, $^1J_{CH}$ = 112.9 Hz, $\underline{CH_2}CH_3$); 32.113 (t, $^1J_{CH}$ = 127.6 Hz, $C_5H_4\underline{CH_2}$); 28.98 (q, $^1J_{CH}$ = 123.9 Hz, $C\underline{Me_3}$); 25.85 (t, $^1J_{CH}$ = 139.8 Hz, C_2H_4); 18.51 (q, $^1J_{CH}$ = 122.5 Hz, $CH_2\underline{CH_3}$).

Synthesis of [C₅H₄(CH₂)₂N-t-Bu]Zr(CH₂CMe₃)₂ (80). A solution of 0.91 g (2.80 mmol) of $[C_5H_4(CH_2)_2N$-*t*-Bu]$ZrCl_2$ and 0.44 g (5.64 mmol) of $LiCH_2CMe_3$ in 30 mL of ether was prepared at -40 °C. The mixture was warmed slowly to room temperature and stirred for 2 h. The solvent was removed in vacuum and the white residue was stripped with 20 mL of pentane. The residue was extracted with 40 mL of pentane and filtered giving a clear colorless solution. The solution was concentrated to 5 mL at room temperature and white crystals were formed on standing overnight at -25 °C. Yield 0.76 g (1.92 mmol, 68%) of $[C_5H_4(CH_2)_2N$-*t*-Bu]$Zr(CH_2CMe_3)_2$. ^1H NMR (300 MHz, C_6D_6): δ 6.25 (m, J_{HH} = 2.57 Hz, 2H, C_5H_4); 6.04 (m, J_{HH} = 2.57 Hz, 2H, C_5H_4); 3.44 (t, $^3J_{HH}$ = 6.41 Hz, 2H, NCH_2); 2.33 (t, $^3J_{HH}$ = 6.41 Hz, 2H, $C_5H_4\underline{CH_2}$); 1.41 (s, 9H, N-*t*-Bu); 1.09 (s, 18H, 2 x $CH_2C\underline{Me_3}$); 1.05 (d, $^2J_{HH}$ = 12.09 Hz, 2H, $\underline{CH_2}CMe_3$); 0.52 (d, $^2J_{HH}$ = 12.09 Hz, 2H, $\underline{CH_2}CMe_3$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 131.85 (s, C_5H_4-*ipso*); 113.53 (d, $^1J_{CH}$ = 169.7 Hz, C_5H_4); 108.13 (d, $^1J_{CH}$ = 172.1 Hz, C_5H_4);

78.84 (t, $^1J_{CH}$ = 103.2 Hz, $\underline{CH_2}CMe_3$); 61.33 (t, $^1J_{CH}$ = 133.7 Hz, NCH_2); 56.42 (s, $N\underline{C}Me_3$); 36.60 (s, $CH_2\underline{C}Me_3$); 35.54 (q, $^1J_{CH}$ = 123.7 Hz, $CH_2C\underline{Me_3}$); 30.25 (t, $^1J_{CH}$ = 128.2 Hz, $C_5H_4\underline{CH_2}$); 29.35 (q, $^1J_{CH}$ = 124.5 Hz, $NC\underline{Me_3}$). IR (cm^{-1}): 3111 (vw), 3100 (vw), 3081 (vw), 2795 (w), 2747 (vw), 2714 (w), 1780 (w), 1748 w), 1730 (w), 1688 (w), 1655 (w), 1636 (w), 1605 (w), 1491 (m), 1468 (m), 1356 (s), 1323 (w), 1231 (s), 1202 (s), 1171 (w), 1076 (s), 1040 (m), 1030 (w), 1017 (vw), 982 (s), 953 (s), 909 (w), 891 (vw), 858 (s), 841 (s), 804 (s), 766 (m), 750 (s), 681 (m), 642 (m), 554 (s), 525 (w), 500 (m), 473 (m), 434 (w). Anal. Calcd for $C_{21}H_{39}NZr$: C, 63.57; H, 9.91; Zr, 22.99. Found: C, 63.41; H, 9.87; Zr, 22.91.

Synthesis of Zr[C$_5$H$_4$(CH$_2$)$_2$N-i-Pr]Ph$_2$ (81). To a cooled (-50 °C) solution of 0.7 g (2.3 mmol) of $Zr[C_5H_4(CH_2)_2N$-*i*-Pr$]Cl_2$ in 50 mL of ether, 4.0 mL (4.6 mmol) of a 1.17 M solution PhMgBr in ether was added. After allowing to warm up to 0 °C in 3 h, the ether was evaporated in vacuum. The yellow brown residue was stripped with 10 mL of pentane. Subsequently, the product was extracted 3 times with 20 mL of pentane. The solution was concentrated and after cooling to -30 °C orange brown crystals precipitated. Yield: 0.4 g (1.0 mmol; 45%). ^{1}H NMR (200 MHz, C_6D_6): δ 7.56 (s, 4H, C_6H_5); 7.06 (m, 6H, C_6H_5); 6.13 (t, 2H, C_5H_4); 5.84 (t, 2H, C_5H_4); 4.44 (m, 1H, $\underline{CH}Me_2$); 3.80 (t, 2H, NCH_2); 2.80 (t, 2H, $C_5H_4\underline{CH_2}$); 0.74 (d, 6H, $CH\underline{Me_2}$) .

Synthesis of Zr[C$_5$H$_4$(CH$_2$)$_2$N-t-Bu]Ph$_2$ (82). To a cooled (-80 °C) solution of 1.3 g (4.0 mmol) of $Zr[C_5H_4(CH_2)_2N$-*t*-Bu$]Cl_2$ in 40 mL of ether, 7 mL (8.2 mmol) of a 1.17 M solution of PhMgBr in ether was added. The mixture was stirred and allowed to warm to room temperature in 2 h and subsequently stirred for another hour. The ether was removed under vacuum and the brown yellow solid was stripped with 10 mL of pentane and extracted 3 times with 25 mL of pentane. The solution was concentrated and after cooling to - 30 °C brown crystals precipitated. The crystals were dried in vacuum and isolated. Yield: 1.21 g (3.0 mmol; 75%). ^{1}H NMR (200 MHz, C_6D_6): δ 7.64 (double d, 4H, C_6H_5); 7.3 - 7.1 (m, 6H, C_6H_5); 5.99 (t, 2H, C_5H_4); 5.85 (t, 2H, C_5H_4); 3.56 (t, 2H, NCH_2); 2.48 (t, 2H, $C_5H_4\underline{CH_2}$); 1.24 (s, 9H, *t*-Bu). ^{13}C NMR (50.3 MHz, C_6D_6): δ 184.4 (s, C_6H_5-*ipso*); 135.3 (d, $^1J_{CH}$ = 155.0 Hz, *m*-C_6H_5); 134.3 (s, C_5H_4-ipso); 127.4 (d, $^1J_{CH}$ = 157.5 Hz, *o*-C_6H_5); 127.3 (d, $^1J_{CH}$ = 156.3 Hz, *p*-C_6H_5); 114.7 (d, $^1J_{CH}$ = 172.1 Hz, C_5H_4); 111.0 (d, $^1J_{CH}$ = 172.1 Hz, C_5H_4); 61.8 (t, $^1J_{CH}$ = 134.3 Hz, NCH_2); 56.3 (s, $\underline{C}Me_3$); 29.9 (t, $^1J_{CH}$ = 127.6 Hz, $C_5H_4\underline{CH_2}$); 27.9 (q, $^1J_{CH}$ = 124.5 Hz, $C\underline{Me_3}$). IR (cm^{-1}): 3047 (sh), 2726 (w), 2673 (w), 1359 (sh), 1343 (sh), 1320 (sh), 1204 (w), 1170 (w), 1058 (m), 1040 (m), 979 (w), 955 (w), 808 (s), 719 (s), 700 (s), 555 (w), 472 (w), 439 (w). Anal. Calcd for $C_{23}H_{27}NZr$: C, 67.59; H, 6.66; Zr, 22.32. Found: C, 66.55; H, 6.70; Zr, 22.52.

Synthesis of Zr[C$_5$H$_4$(CH$_2$)$_2$N-t-Bu](Ph-d$_5$)$_2$ (82-d$_{10}$). Using the same procedure as for the synthesis of **82**, 1.4 g (3.3 mmol) of $Zr[C_5H_4(CH_2)_2N$-*t*-Bu$]Cl_2$ was reacted with 11.7 mL (6.8 mmol) of a 0.58 M solution of Ph-d_5MgBr in ether. After work-up brown crystals were obtained. Yield: 0.7 g (1.6 mmol; 45%). ^{1}H NMR (200 MHz, C_6D_6): δ 5.99 (t, 2H, C_5H_4); 5.85 (t, 2H, C_5H_4); 3.56 (t, 2H, $C_5H_4CH_2$); 2.48 (t, 2H, CH_2N); 1.24 (s, 9H, $C(CH_3)_3$. ^{13}C NMR (50.3 MHz, C_6D_6); δ 184.2 (s, C_6H_5-*ipso*), 135.2 (s, *m*-

C_6H_5), 134.9 (s, C_5H_4-ipso), 128.0 (s, *o*-C_6H_5), 127.7 (s, *p*-C_6H_5), 114.7 (d, $^1J_{CH}$ = 170.9 Hz, C_5H_4), 111.0 (d, $^1J_{CH}$ = 172.1 Hz, C_5H_4), 61.7 (t, $^1J_{CH}$ = 133.6 Hz, NCH_2), 56.3 (s, $\underline{C}Me_3$), 29.9 (t, $^1J_{CH}$ = 128.2 Hz, $C_5H_4\underline{CH_2}$), 27.9 (q, $^1J_{CH}$ = 124.6 Hz, $C\underline{Me_3}$). IR (cm^{-1}): 3076 (sh), 2726 (w), 2673 (w), 2350 (w), 2259 (m), 2224 (w), 2210 (w), 1359 (sh), 1343 (sh), 1325 (sh), 1243 (w), 1203 (m), 1091 (m), 948 (m), 808 (s), 766 (m), 617 (m), 528 (s), 470 (m).

Synthesis of [$C_5H_4(CH_2)_2$NMe]Zr(CH_2Ph)$_2$ (83). A solution of 1.98 g (4.34 mmol) of $Zr(CH_2Ph)_4$ in 20 mL of toluene was treated with 0.55 g (4.46 mmol) of $C_5H_5(CH_2)_2$ N(H)Me and the mixture was stirred overnight at 50 ^oC, yielding a brown solution. The solvent was removed in vacuum and the remaining oily residue was stripped with pentane. The residue was extracted with 40 mL of ether and filtered. The solution was concentrated to 10 mL and cooled overnight to -25 ^oC. Brown-yellow crystals were obtained. Yield: 0.38 g (0.96 mmol, 22%) of $[C_5H_4(CH_2)_2NMe]Zr(CH_2Ph)_2$. ^1H NMR (300 MHz, C_6D_6): δ 7.11 (t, $^3J_{HH}$ = 7.69 Hz, 4H, *m*-Ph); 6.92 (t, $^3J_{HH}$ = 7.32 Hz, 2H, *p*-Ph); 6.47 (d, $^3J_{HH}$ = 7.69 Hz, 4H, *o*-Ph); 5.72 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 5.28 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 3.43 (t, $^3J_{HH}$ = 6.78 Hz, 2H, NCH_2); 2.49 (s, 3H, NMe); 2.43 (t, $^3J_{HH}$ = 6.78 Hz, 2H, $C_5H_4\underline{CH_2}$); 1.44 (d, $^2J_{HH}$ = 9.16 Hz, 2H, Ph$\underline{CH_2}$); 1.36 (d, $^2J_{HH}$ = 9.16 Hz, 2H, Ph$\underline{CH_2}$). ^{13}C NMR (75.4 MHz, $C_6D_6$146.14 (s, Ph-*ipso*); 135.93 (s, C_5H_4-*ipso*); 130.56 (d, $^1J_{CH}$ = 157.5 Hz, *o*-Ph); 125.15 (d, $^1J_{CH}$ = 155.0 Hz, *m*-Ph); 121.80 (d, $^1J_{CH}$ = 161.1 Hz, *p*-Ph); 112.92 (d, $^1J_{CH}$ = 170.9 Hz, C_5H_4); 107.80 (d, $^1J_{CH}$ = 170.9 Hz, C_5H_4); 71.37 (t, $^1J_{CH}$ = 134.3 Hz, NCH_2); 50.85 (t, $^1J_{CH}$ = 129.4 Hz, $\underline{CH_2}$Ph); 37.16 (q, $^1J_{CH}$ = 133.1 Hz, NMe); 28.89 (t, $^1J_{CH}$ = 127.6 Hz, $C_5H_4\underline{CH_2}$). IR (cm^{-1}): 3055 (w), 3005 (w), 2809 (w), 2772 (m), 2674 (w), 1589 (s), 1557 (w), 1478 (s), 1445 (m), 1410 (w), 1348 (vw), 1327 (w), 1298 (w), 1231 (m), 1213 (s), 1192 (m), 1181 (m), 1157 (w), 1113 (s), 1088 (w), 1065 (w), 1047 (m), 1038 (w), 1028 (m), 1005 (s), 978 (s), 964 (m), 903 (m), 868 (m), 837 (s), 810 (vs), 745 (s), 696 (s), 644 (w), 556 (m), 546 (m), 511 (s), 424 (s). Anal. Calcd for $C_{22}H_{25}NZr$: C, 66.95; H, 6.39; Zr, 23.11. Found: C 66.71; H, 6.46; Zr, 23.04.

Synthesis of [$C_5H_4(CH_2)_2$N-*i*-Pr]Zr(CH_2Ph)$_2$ (84). To a cooled (0 ^oC) solution of 1.33 g (2.92 mmol) of $Zr(CH_2Ph)_4$ in 10 mL of toluene, 446 µL (2.99 mmol) of $C_5H_5(CH_2)_2N(H)$-*i*-Pr was added. The mixture was stirred overnight at ambient temperature. After removal of the solvent the sticky residue was stripped with 10 mL of pentane leaving a brown powder which was extracted with ether. Upon concentrating the solution and standing overnight at -20 ^oC 0.55 g crystalline material was obtained. A second crop yielded 0.25 g of product. Total yield: 0.80 g (1.89 mmol, 65%) of $[C_5H_4(CH_2)_2N$-*i*-Pr]Zr(CH_2Ph)$_2$. ^1H NMR (300 MHz, C_6D_6): δ 7.12 (t, ^3J_H = 7.69 Hz, 4H, *m*-Ph); 6.94 (t, $^3J_{HH}$ = 7.32 Hz, 2H, *p*-Ph); 6.58 (d, $^3J_{HH}$ = 7.32 Hz, 4H, *o*-Ph); 5.72 (t, $^3J_{HH}$ = 2.57 Hz, 2H, C_5H_4); 5.27 (t, $^3J_{HH}$ = 2.57 Hz, 2H, C_5H_4); 3.57 (h, $^3J_{HH}$ = 6.04 Hz, 1H, $\underline{CH}Me_2$); 3.48 (t, $^3J_{HH}$ = 6.59 Hz, 2H, NCH_2); 2.44 (t, $^3J_{HH}$ = 6.59 Hz, 2H, $C_5H_4\underline{CH_2}$); 1.67 (d, $^2J_{HH}$ = 9.15 Hz, 2H, Ph$\underline{CH_2}$); 1.05 (d, $^2J_{HH}$ = 9.15 Hz, 2H, Ph$\underline{CH_2}$); 0.94 (d, $^2J_{HH}$ = 6.23 Hz, 6H, CHMe_2). ^{13}C NMR (75.4 MHz, C_6D_6): δ 146.53 (s, *ipso*-Ph); 135.83 (s, *ipso*-C_5H_4); 130.32 (d, $^1J_{CH}$ = 157.5 Hz, *o*-Ph); 125.59 (d, $^1J_{CH}$ = 153.8 Hz, *m*-Ph); 121.85 (d, $^1J_{CH}$ = 162.4 Hz, *p*-Ph); 113.06 (d, $^1J_{CH}$ = 170.9 Hz, C_5H_4); 108.64 (d, $^1J_{CH}$ = 170.9 Hz, C_5H_4); 59.89 (t, $^1J_{CH}$ = 130.0 Hz, CH_2Ph); 50.34 (t, $^1J_{CH}$ = 128.2 Hz, NCH_2); 44.95 (d, $^1J_{CH}$ = 120.9 Hz, $CH(CH_3)_2$); 29.39 (t,

$^1J_{CH}$ = 127.6 Hz, $C_5H_4CH_2$); 21.32 (q, $^1J_{CH}$ = 125.7 Hz, $CH(CH_3)_2$). IR (cm^{-1}): 3063 (w), 3046 (m), 3005 (m), 2683 (w), 2670 (w), 1659 (w), 1643 (w), 1632 (w), 1589 (s), 1559 (m), 1489 (sh, 1478 cm^{-1}), 1478 (s), 1460 (m), 1445 (m), 1418 (m), 1393 (s), 1358 (m), 1343 (m), 1319 (vw), 1298 (m), 1279 (m), 1265 (w), 1246 (w), 1231 (m), 1211 (s), 1190 (m), 1175 (m), 1159 (m), 1146 (w), 1105 (m), 1088 (w), 1067 (w), 1053 (s), 1036 (m), 1026 (s), 1005 (m), 991 (m), 978 (s), 899 (s), 872 (w), 837 (m) (824 (s), 804 (s), 745 (s), 704 (m), 696 (s), 644 (m), 610 (w), 594 (vw), 542 (m), 517 (s), 448 (m), 428 (m), 415 (s). Anal. Calcd for $C_{24}H_{29}NZr$: C, 68.19; H, 6.92; Zr, 21.58. Found: C, 68.44; H, 7.15; Zr, 21.47.

Synthesis of Zr[C₅H₄(CH₂)₂N-t-Bu](CH₂Ph)₂ (85). To a cooled solution (- 40 °C) of 1.7 g (5.2 mmol) of $Zr[C_5H_4(CH_2)_2N$-*t*-$Bu]Cl_2$ in ether, 7.8 mL (10.5 mmol) of a 1.35 M solution of $PhCH_2MgBr$ in ether was quickly added. The mixture was stirred and allowed to warm to room temperature in 3 h. The ether was evaporated in vacuum and the yellow solid residue stripped with 15 mL of pentane. The product was extracted 3 times with 40 mL of pentane. The solution was concentrated and after cooling to - 30 °C brown crystals precipitated. Yield: 1.5 g (3.4 mmol; 65%). ^{1}H NMR (200 MHz, C_6D_6): δ 7.11 (t, 4H, C_6H_5); 6.93 (t, 2H, C_6H_5); 6.70 (t, 4H, C_6H_5); 5.57 (t, 2H, C_5H_4); 5.47 (t, 2H, C_5H_4); 3.35 (t, 2H, CH_2N); 2.24 (t, 2H, $C_5H_4\underline{CH_2}$); 1.94 (d, 1H, $Ph\underline{CH_2}$); 1.43 (d, 1H, $Ph\underline{CH_2}$); 1.13 (s, 9H, *t*-Bu). ^{13}C NMR (75.4 MHz, C_6D_6): δ 146.24 (s, *ipso*-Ph); 134.80 (s, C_5H_4-*ipso*); 129.28 (d, $^1J_{CH}$ = 156.3 Hz, *o*-Ph); 126.96 (d, $^1J_{CH}$ = 155.0 Hz, *m*-Ph); 121.79 (d, $^1J_{CH}$ = 162.4 Hz, *p*-Ph); 113.60 (d, $^1J_{CH}$ = 170.9 Hz, C_5H_4); 110.98 (d, $^1J_{CH}$ = 172.1 Hz, C_5H_4); 61.49 (t, $^1J_{CH}$ = 134.3 Hz, NCH_2); 56.84 (s, $\underline{C}Me_3$); 52.86 (t, $^1J_{CH}$ = 124.5 Hz, $Ph\underline{CH_2}$); 29.90 (t, $^1J_{CH}$ = 127.6 Hz, $C_5H_4\underline{CH_2}$); 28.02 (q, $^1J_{CH}$ = 124.5 Hz, CMe_3). IR (cm^{-1}): 3169 (sh), 3152 (sh), 3138 (sh), 3131 (sh), 2726 (w), 2675 (w), 1593 (m), 1379 (s), 1302 (sh), 1208 (w), 1169 (w), 980 (m), 810 (s), 793 (s), 766 (m), 536 (w), 519 (w). Anal. Calcd for $C_{25}H_{31}NZr$: C, 68.75; H, 7.15; Zr, 20.89. Found: C, 68.39; H, 7.10; Zr, 20.80.

Synthesis of [C₅H₄(CH₂)₃NEt]Zr(CH₂Ph)₂ (87). To a cooled (0 °C) suspension of 1.63 g (5.24 mmol) of $[C_5H_4(CH_2)_3NEt]ZrCl_2$ in 30 mL of ether, 11.4 mL of a 0.93 M solution of $PhCh_2MgCl$ in ether was added. On warming to room temperature the mixture became light yellow. After stirring for 3 h at room temperature the solvent was removed in vacuum and the light yellow residue stripped with 30 mL of pentane. The solids were extracted with 40 mL of hot hexane. Concentrating the hot solution to ± 10 mL and cooling to 0 °C yielded 1.44 g (3.41 mmol, 65%) $[C_5H_4(CH_2)_3NEt]Zr(CH_2Ph)_2$. ^{1}H NMR (300 MHz, C_6D_6): δ 7.11 (t, $^3J_{HH}$ = 7.51 Hz, 4H, *m*-Ph); 6.94 (t, $^3J_{HH}$ = 7.32 Hz, 2H, *p*-Ph); 6.61 (d, $^3J_{HH}$ = 7.33 Hz, 4H, *o*-Ph); 5.60 (m, J_{HH} = 2.75 Hz, 2H, C_5H_4); 5.39 (m, J_{HH} = 2.57 Hz, 2H, C_5H_4); 3.05 (q, $^3J_{HH}$ = 6.47 Hz, 2H, $N\underline{CH_2}CH_3$); 2.45 (m, 2H, NCH_2); 2.21 (m, 2H, $C_5H_4\underline{CH_2}$); 1.62 (d, $^2J_{HH}$ = 9.52 Hz, 2H, $Ph\underline{CH_2}$); 1.53 (m, 2H, $NCH_2\underline{CH_2}$); 1.22 (d, $^2J_{HH}$ = 9.52 Hz, 2H, $Ph\underline{CH_2}$); 1.00 (t, $^3J_{HH}$ = 6.47 Hz, 3H, $NCH_2\underline{CH_3}$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 145.66 (s, Ph-*ipso*); 129.51 (d, $^1J_{CH}$ = 157.5 Hz, *o*-Ph); 126.30 (d, $^1J_{CH}$ = 153.8 Hz, *m*-Ph); 122.69 (s, C_5H_4-*ipso*); 121.82 (d, $^1J_{CH}$ = 110.64 (d, $^1J_{CH}$ = 170.9 Hz, C_5H_4); 110.31 (d, $^1J_{CH}$ = 170.9 Hz, C_5H_4); 50.72 (t, $^1J_{CH}$ = 132.5 Hz, $N\underline{CH_2}CH_3$); 49.61 (t, $^1J_{CH}$ = 127.6 Hz, $Ph\underline{CH_2}$); 39.66 (t, $^1J_{CH}$= 127.6 Hz, NCH_2); 30.11 (t, $^1J_{CH}$ = 126.4 Hz, $C_5H_4CH_2$); 26.77 (t, $^1J_{CH}$ = 125.7 Hz, $NCH_2\underline{CH_2}$); 14.89 (q, $^1J_{CH}$ = 126.6 Hz, $NCH_2\underline{CH_3}$), IR (cm^{-1}): 3117 (w), 3088 (m),

3079 (m), 3065 (w), 2756 (w), 2712 (w), 2677 (w), 2004 (w), 1930 (vw), 1832 (vw), 1782 (vw), 1753 (vw), 1667 (vw), 1589 (s), 1539 (vw), 1479 (s), 1445 (s), 1422 (w), 1400 (w), 1364 (w), 1350 (m), 1302 (m), 1271 (w), 1231 (m), 1209 (s), 1179 (s), 1163 (m), 1123 (m), 1088 (w), 1072 (w), 1053 (w), 1036 (s), 1007 (s), 980 (s), 939 (m), 907 (s), 893 (w), 864 (s), 841 (m), 795 (vs), 746 (vs), 696 (vs), 662 (m), 606 (m), 571 (m), 552 (m), 542 (m), 523 (s), 433 (s).

Synthesis of [$C_5H_4(CH_2)_3$N-i-Pr]Zr($CH_2Ph)_2$ (88). A cooled suspension (-20 ^oC) of 2.13 g (6.55 mmol) [$C_5H_4(CH_2)_3$N-*i*-Pr]$ZrCl_2$ in 30 mL of ether was treated with 15 mL 0.93 M (13.9 mmol) $PhCH_2MgCl$ in ether. After warming to room temperature the mixture was stirred for 4 h while the colorless mixture turned light yellow. Removal of the solvent yielded a light yellow residue which was stripped with 30 mL of pentane. The solids were extracted with 50 mL of pentane and the resulting light yellow solution was concentrated to 15 mL. Light yellow crystals were obtained on standing overnight at -20 ^oC. 1.92 g of product was isolated. A second crop (0.51 g) was obtained. Total yield: 2.43 g (5.56 mmol. 85%) of [$C_5H_4(CH_2)_3$N-*i*-Pr)Zr($CH_2Ph)_2$. ^{1}H NMR (300 MHz, C_6D_6): δ 7.14 (t, $^3J_{HH}$ = 7.69 Hz, 4H, *m*-Ph); 6.95 (t, $^3J_{HH}$ = 7.33 Hz, 2H, *p*-Ph); 6.70 (d, $^3J_{HH}$ = 7.32 Hz, 4H, *o*-Ph); 5.59 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 5.30 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 4.00 (hp, $^3J_{HH}$ = 5.77 Hz, 1H, $\underline{CH}Me_2$); 2.50 (m, 2H, NCH_2); 2.23 (m, 2H, $C_5H_4\underline{CH_2}$); 1.86 (d, $^2J_{HH}$ = 9.52 Hz, 2H, $Ph\underline{CH_2}$); 1.58 (m, 2H, $NCH_2\underline{CH_2}$); 1.12 (d, $^3J_{HH}$ = 5.86 Hz, 6H, $CH\underline{Me_2}$); 1.01 (d, $^2J_{HH}$ = 9.52 Hz, 2H, $Ph\underline{CH_2}$). ^{13}C NMR (75.4 MHz, C_6D_6): δ 146.51 (s, Ph-*ipso*); 129.39 (d, $^1J_{CH}$ = 157.5 Hz, *o*-Ph); 126.53 (d, $^1J_{CH}$ = 153.8 Hz, *m*-Ph); 122.63 (s, C_5H_4-*ipso*); 121.77 (d, $^1J_{CH}$ = 161.1 Hz, *p*-Ph); 111.43 (d, $^1J_{CH}$ = 170.9 Hz, C_5H_4); 110.75 (d, $^1J_{CH}$ = 169.7 Hz, C_5H_4); 50.98 (t, $^1J_{CH}$ = 125.1 Hz, $Ph\underline{CH_2}$); 43.49 (t, $^1J_{CH}$ = 132.5 Hz, NCH_2); 42.07 (d, $^1J_{CH}$ = 114.8 Hz, $\underline{CH}Me_2$); 30.84 (t, $^1J_{CH}$ = 126.4 Hz, $C_5H_4\underline{CH_2}$); 27.06 (t, $^1J_{CH}$ = 127.0 Hz, $NCH_2\underline{CH_2}$); 21.59 (q, $^1J_{CH}$ = 126.1 Hz, $CH\underline{Me_2}$). IR (cm^{-1}): 3109 (m), 3063 (w), 3007 (w), 2701 (w), 2679 (w), 2656 (m), 1954 (w), 1941 (w), 1917 (w), 1834 (w), 1790 (w), 1759 (w), 1707 (w), 1661 (w), 1591 (s), 1562 (sh, 1661 cm^{-1}), 1478 (m) 1447 (m), 1362 (s), 1335 (w), 1300 (w), 1275 (w), 1260 (w), 1236 (m), 1213 (s), 1182 m), 1171 (w), 1113w), 1088 (m), 1065 (m), 1051 (w), 1028 (m), 1015 (m), 986 (s), 934 (m), 907 (m), 860 (s), 806 (s), 745 (s), 700 (s), 664 (w), 604 m), 557 (m), 546 (w), 519 (m), 446 w), 420 (s).

Synthesis of [$C_5H_4(CH_2)_3$N-t-Bu]Zr($CH_2Ph)_2$ (89). A cooled (0 ^oC) suspension of 0.40 g (1.18 mmol) of [$C_5H_4(CH_2)_3$N-*t*-Bu]$ZrCl_2$ in 20 mL of ether was treated with 2.7 mL 0.93 M (2.51 mmol) of $PhCH_2MgCl$ in ether and stirred for 3 h at room temperature. The mixture became yellow. The solvent was removed in vacuum and the yellow residue was stripped with 20 mL of pentane. The residue was extracted twice with 40 mL of pentane. The resulting yellow solution was concentrated to 10 mL and transferred into a small vessel. Evaporation of the solvent left an orange oil. Yield: 0.41 g (0.91 mmol, 77%) of [$C_5H_4(CH_2)_3$N-*t*-Bu]Zr($CH_2Ph)_2$. ^{1}H NMR (300 MHz, C_6D_6): δ 7.21 (t, $^3J_{HH}$ = 7.69 Hz, 4H, *m*-Ph); 6.92 (overlapped resonances: d, $^3J_{HH}$ = 8.42 Hz, 4H, *o*-Ph; 2H, *p*-Ph); 5.79 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 5.52 (m, J_{HH} = 2.56 Hz, 2H, C_5H_4); 2.58 (m, 2H, $C_5H_4\underline{CH_2}$); 2.15 (d, $^2J_{HH}$ = 10.62 Hz, 2H, $Ph\underline{CH_2}$); 2.10 (m, 2H, NCH_2); 1.96 (d, $^2J_{HH}$ = 10.62 Hz, 2H, $PhCH_2$); 1.31 (m, 2H, $NCH_2\underline{CH_2}$); 1.20 (s, 9H, *t*-Bu). ^{13}C NMR (75.4 MHz, C_6D_6): δ 149.04 (s, Ph-*ipso*); 128.74 (d, $^1J_{CH}$ = 156.3 Hz, *o*-Ph);

126.66 (d, $^1J_{CH}$ = 153.8 Hz, *m*-Ph); 126.60 (s, C_5H_4-*ipso*); 121.45 (d, $^1J_{CH}$ = 157.5 Hz, *p*-Ph); 114.83 (d, $^1J_{CH}$ = 172.1 Hz, C_5H_4); 112.55 (d, $^1J_{CH}$ = 169.7 Hz, C_5H_4); 63.53 (t, $^1J_{CH}$ = 119.6 Hz, Ph$\underline{CH_2}$); 57.08 (s, $\underline{C}Me_3$); 48.22 (t, $^1J_{CH}$ = 132.5 Hz, NCH_2); 34.14 (t, $^1J_{CH}$ = 126.4 Hz, $C_5H_4\underline{CH_2}$); 29.65 (q, $^1J_{CH}$ = 124.9 Hz, $C\underline{Me_3}$); 28.02 (t, $^1J_{CH}$ = 127.0 Hz, $NCH_2\underline{CH_2}$). IR (cm^{-1}, neat): 3069 (m), 3015 (m), 2963 (s), 2924 (s), 2855 (s), 2774 (w), 1933 (w), 1848 (w), 1792 (w), 1721 (w), 1665 (w), 1593 (vs), 1537 (w), 1483 (s), 1449 (m), 1387 (m), 1358 (s), 1300 (vw), 1277 (w), 1252 (m), 1206 (vs), 1154 (vw), 1096 (m), 1071 (m), 1030 (s), 1011 (m), 988 (s), 937 (m), 885 (m), 862 (m), 808 (vs), 746 (vs), 698 (vs), 610 (w), 559 (m), 519 (m).

5.11 References and Notes.

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